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THE FIFTEENTH JOHN MERCER LECTURE

Aspects of Pigment Dispersion related to Usage

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Meeting held at the Charing Cross Hotel, London, on 1st May 1959, Mr. John Boulton (President of the Society) in the chair

Optical and fastness properties are of limited value unless satisfactory dispersion of a pigment can be achieved and maintained. In aqueous systems dispersion and stabilisation can be effected by soluble surface-active agents, but in non-aqueous media the degree of stabilisation is much lower. Dispersion of pigments into viscose solution is best achieved by minimising differences existing at the mixing boundary. In pigment printing compositions fineness of particles affects both fabric penetration and pigment binding. Stabilisation of yellow organic pigments with non-ionic agents is necessary to avoid coagulation of emulsion paints. In non-aqueous systems mixing procedures are most efficient when conditions allow maximum contribution by the pigment to its own dispersion. The degree of particle flocculation existing in a printing ink is a controlling factor in its behaviour on the paper surface. Seeding arising from milling high-pigment–low-resin paint compositions can be reduced by lowering the differential resin concentration at the dilution boundary. Variations in depth of colour caused by differences in film-forming conditions for paints containing phthalocyanine blue are substantially overcome by surface treatment to reduce flocculation.

Introduction

John Mercer is commonly remembered for his experiments on the treatment of cotton with caustic soda, but his interests were wide and diverse. The initial impetus which set him off on a career of investigation and invention came from the vivid impression that a beautifully coloured fabric made on him. Once aroused, his avid curiosity, aided by his ability as an experimenter, led him into a multiplicity of studies. His many discoveries included the development of a new method for fixing Prussian Blue (C.I. Pigment Blue 27) on cloth, the application of Antimony Orange (C.I. Pigment Red 107), and the introduction of alumina lakes of dyes for steam colour work. His interest in insoluble coloured compounds, therefore, provides some connection with the present subject of pigments. Since his day, the development of synthetic organic dyes has provided many new ranges of brilliant colorants with improved fastness properties, and from the same fields of chemistry have come also the great majority of organic pigments. Although initially their use lay essentially in non-textile fields, such as paints, printing inks, and rubber, selected chemical types are now extensively used in the coloration of textiles.

Like a good soluble dye, a good pigment must efficiently provide the desired change in visual appearance and subsequent resistance to destruction. But, in the case of a pigment, colour and fastness are of limited value if a satisfactory dispersion cannot be produced and maintained. So many important properties are bound up with the dispersion characteristics of a pigmented system that, in recent years, this field has been investigated by the manufacturer and the user at least as much as the fields of optical and fastness properties. It was this trend which suggested a basis for bringing together selected problems from the several pigment-consuming industries for this lecture. From the many pigment–binder combinations which exist, I have therefore chosen illustrations of practical behaviour which are concerned essentially with degree and state of pigment dispersion, with some special emphasis on the time factor.

During the past decade, specialised physical forms of both pigment powders and pastes have been growing in usage wherever the demand has warranted their development. With these, successful application in one medium, or perhaps a small group of media, is often achieved at the expense of optimum properties for other uses. Non-specialised forms of pigment, on the other hand, can obviously give rise to dispersion problems resulting from imperfections in the compromise of properties. In non-aqueous systems, where there is a great

multiplicity of media, a semi-empirical approach to such problems has normally to be employed. This may be of considerable immediate value, but the gap between it and the fundamental approach is very wide and the reason is not difficult to find. Whereas scientific techniques are available for fundamental measurements to be made on simple systems, such as size-graded particles of pure silica in benzene, similar techniques cannot yet be applied to more complex systems such as a pigmented viscose solution or a synthetic stoving enamel. Furthermore, many practical systems are far from a state of true equilibrium, and the pigments, media, extenders, solvents, and numerous other additives seldom if ever approach pure compounds. Apart from the presence of moisture, electrolyte, and traces of by-products which remain in all pigments, deliberate surface treatment to improve performance has become relatively common practice. In a similar way, practical media and solvents are usually mixtures of compounds varying in molecular weight, chemical type, and impurity content.

With such a picture of the real raw materials used, it is no wonder that so many unsolved mysteries are recorded in the notebooks of technologists. In spite of this, some understanding of the more fundamental aspects as they can be seen today is of undoubted value as a background to examples of practical behaviour.

Theoretical Concepts

When a solid surface is being wetted by a liquid, work must be done if the energy of the new interface is greater than that of the original one. If the reverse is true, work will be done by the liquid, and heat may be liberated in consequence. The important property of adhesion tension, defined by Freundlich, represents the difference between the surface tension of the solid itself and the interfacial tension of the liquid–solid interface. Thus a low interfacial tension corresponds to a high adhesion tension and to a less abrupt change in energy across the liquid–solid interface.

Adsorption of molecules of a pure liquid, or of some component of a more complex liquid, occurs when the surface of a solid is wetted to give a lower interfacial energy. In some cases irreversible adsorption by chemical combination may take place, e.g. a basic pigment reacting with a fatty acid. More often, reversible amphipathic adsorption of a compound occurs by orientation at the surface; e.g. in water a hydrophobic surface will strongly adsorb an amphipathic substance, i.e. one containing both a hydrophobic group capable of being adsorbed on the surface and a hydrophilic group solvated in water.

Complete stabilisation of a colloidal suspension is considered to be attained when particles show no net force of attraction for each other, and in this form the suspension is fully deflocculated. The range of sizes for practical pigment dispersions varies considerably from pigment to pigment, but extends effectively from a diameter of 0·01 to 2·0 μ. Between such particles van der Waals–London forces will cause an attraction depending on the distance between particles and their size and nature. Stabilisation–deflocculation, therefore, requires that such forces are rendered ineffective.

In aqueous systems stabilisation of a flocculated suspension can be achieved by adsorption of amphipathic ions to form an electrical double layer, e.g. an anionic agent. The adsorbed layer is balanced by an equal, but more diffuse, layer of opposite charge in the aqueous phase. If such adsorption provides a net force of repulsion, or no force at all, particles will behave independently and will settle gradually to a low sediment volume. A protective colloid carrying electrical charges can also stabilise a suspension by a similar mechanism and, in addition, its high molecular weight prevents rapid desorption and can contribute temporary stability by lowering the mobility of particles. Stabilisation can be effected also by adsorption from solution of unionised compounds containing powerful hydrophilic groupings, e.g. polyethenoxy chains, attached to hydrophobic groups such as alkyl chains. Amphipathic adsorption then creates a sheath of strongly adsorbed molecules round each particle, and although there is no net force of repulsion, such a layer can considerably reduce the force of attraction by preventing close approach of particles. The overall result in each type of stabilisation is a reduction in the abruptness of the energy change across the interface.

In non-aqueous media comparable theoretical concepts have been worked out, but the degree to which the ionic mechanism can be effective is considered to be extremely small. Nevertheless, amphipathic adsorption of compounds containing lyophilic and lyophobic groups occurs, with solvation of external groups of the adsorbed layer. The degree of stabilisation achieved will depend on how far the net force of attraction between particles can be made ineffective by presence of the surface layer. More recently, Koelmans and Overbeek [1] have concluded that in media of low polarity modest electrical charges and zeta potential are adequate to stabilise particles of size greater than 1 μ. At the same time hardly any stabilisation could be expected from non-ionised long-chain molecules. They have calculated that below 1 μ. the potential barrier necessary for stabilisation cannot be established and that, for stabilisation by steric hindrance, a non-ionised adsorbed layer would need to keep the particles from approaching closer than one diameter.

The precise mechanism of flocculation–deflocculation effects has yet to be explained. Indirectly, the flocculated nature of a suspension may be observed by such well known characteristics as thixotropic flow behaviour or sedimentation volume. Both these effects point to the existence of rigidity in the structural units, making them more analogous to rods than to the commonly used description of chains. Furthermore, the low volume concentration at which a highly flocculated pigment suspension shows no fluidity, or settles to a minimum volume, requires that the degree of anisometry of structural units is high. In practice, the equilibrium sediment volume in water of a highly flocculated organic pigment may correspond

to a volume concentration of only a few per cent. Additions of increasing amounts of anionic dispersing agent will reduce the sediment volume; yet over a wide range the pigment is still flocculated. In a fully deflocculated suspension no structural units exist, and there is nothing to prevent settling into as close packing as the stabilising forces will allow.

This picture of rod-like units suggests that in flocculation there must be a definite tendency for a third particle, approaching two which are already in contact, to position itself so as to elongate the unit. In addition, the greater surface area of smaller particles provides a much greater possibility of structure formation, since the potential number of particle–particle contacts increases rapidly with decrease in particle size.

Aqueous Systems

A. MASS-PIGMENTATION OF VISCOSE RAYON

Manufacture of the viscose rayon fibre commences with solubilisation of cellulose in water by conversion of its alcohol groups to xanthate groups by the action of caustic soda and carbon disulphide. This results in a highly viscous solution of sodium cellulose xanthate as a hydrated poly-electrolyte carrying a weak negative charge. From the time of completion of solution and removal of carbon disulphide, the solubilising reaction starts to operate in the reverse direction. As a result, cellulose is regenerated in a hydrated condition by hydrolysis, and forms micelle ions with the more strongly hydrated xanthate. Such emulsoidal particles of hydrated cellulose are essential for sufficiently rapid coagulation to occur when the viscose is extruded during spinning into an acidic solution of concentrated electrolyte. In the external continuous phase is a colloidal solution of xanthate containing electrolytes formed as by-products of the reaction. Lower viscosity, which is advantageous in pumping, is obtained by the addition of caustic soda solution, which, going into the continuous phase, effectively dehydrates the micelles by raising their osmotic pressure.

Several filtrations are necessary during the process to remove undissolved or recoagulated material, which could block spinneret holes or interfere with the properties of the filament produced. The final gear pump maintains a constant-volume flow of viscose through the last fine filter to the spinneret, and, as the process proceeds, the pump works at increasing pressure, since the viscose is increasing in viscosity and the filter cloth itself is blocking gradually as it takes out unwanted particles.

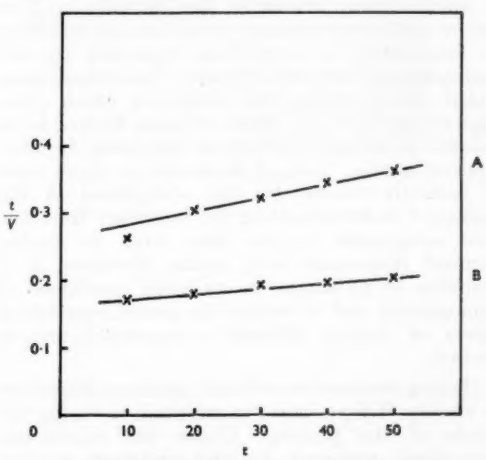
The production of mass-pigmented viscose rayon therefore necessitates the preparation of a suspension of particles small enough to pass through fine filters. Such a condition immediately sets a limit to the size of particle which can reach the final filament, and as the final filter has an effective pore size of the order of 2–3 μ., the general order of particle size needs to be substantially lower. Any pigment particles retained by the filter will contribute an additional blocking effect to that resulting from the viscose itself, and consequently will necessitate even higher pumping pressures. As much pigment as possible must pass the filter, therefore, but particles reaching the filament must not be large enough to affect physical properties or to interfere with the fibre surface. Although the spinneret holes are relatively large, e.g. 50 μ., the finest filaments of 1·5 denier have an approximate diameter of 12·5 μ. Pigment dispersions containing a very high proportion of extremely fine particles are therefore used (Fig. 1). In practice, the range 0·1–1·0 μ. provides high tinctorial strength for a given weight of pigment, and thereby reduces the quantity needed to obtain a given depth of colour. This correspondingly reduces filtration problems (provided that particles are maintained in ultimate dispersion), and gives minimum interference with the physical properties of the fibre.

Because of its importance, filterability measurement has become a well established laboratory procedure and has received much attention. The original investigators, P. H. Hermans *et al.*[2], were concerned with the viscose solution itself, where different types of filtration behaviour could be expressed mathematically. In the most common type, particles are considered to be filtered out by deposition on the surfaces forming the pores of the filter, and such a mechanism is the basis for the standard equation—

$$\tfrac{1}{2}\,kt = \frac{t}{V} - \frac{1}{S_0}$$

where t = time in min., V = volume of filtered viscose, S_0 = initial porosity of the filter, and k = a constant.

Where behaviour conforms to this equation, practical measurements on the volume of suspension passing through a standard filter at constant pressure will provide a straight-line graph on plotting t/V against t, the slope of which can be related to a constant K, for convenience multiplying k by 1000. The higher the K value, the worse is the filter-blocking tendency of the suspension, and typical graphs shown in Fig. 2 illustrate this behaviour.



A— Monastral Fast Blue BVS (C.I. Pigment Blue 15), K = 25
B— Monolite Red 4RHVS (C.I. Pigment Red 7), K = 7·5

FIG. 2—Typical Filterability Curves

Apart from the ultimate particle size factor, any occurrence of particle agglomeration before or after passing the final filter will be of significance. The pastes used therefore contain combinations of surface-active agents, principally of anionic or non-ionic types, which are chosen to facilitate incorporation of the pigment and to provide as fine and as stable a dispersion as possible in the viscose solution. Consideration of the stabilising mechanism of these two classes of surface-active agent make it remarkable that either type can be used successfully. Pigment suspensions stabilised with anionic agents can be flocculated by means of electrolytes, which exist in appreciable quantities in the viscose solution. Non-ionic agents, on the other hand, although less susceptible to the action of electrolyte, need to possess a high degree of hydration to be effective. In viscose this will be opposed by the strongly hydrophilic nature of the cellulose xanthate, reinforced by the action of other electrolytes present.

During the incorporation process, therefore, the mixing of a fluid, highly deflocculated pigment suspension into a viscous solution having powerful flocculating action must be carried out so as to minimise the potential loss in degree of pigment dispersion. The preferred method of mixing is to add viscose solution gradually to the pigment paste, rather than *vice versa*, since, in practice, the latter method can result in relatively large agglomerates of pigment particles which cannot be fully dispersed even by prolonged mixing (Fig. 3). This is principally due to the time factor involved. Homogenisation of the two fluids proceeds at a rate depending on the efficiency of the mixer, and in the initial stages gross layers of paste and viscose are present, which further break down as mixing continues, so that in absence of any change in fluidity of the components the system eventually reaches homogeneity. When pigment paste is added to viscose, diffusion initially occurring across the boundary results in the formation of dense flocculates resistant to the action of the mixer. With the reverse procedure, the flocculating effect of alkali in the viscose is low initially, and as viscose addition continues the increasing tendency to flocculation is more than balanced by the increasing concentration of protective colloid being added, thus avoiding the conditions which cause agglomeration. Such effects will later be seen to be parallel to certain difficulties occurring in non-aqueous media. Loss of dispersion in these cases is basically caused by the abruptness of the change of state in crossing the boundary from one fluid component to the other and, in mixing pigment dispersions with media, therefore, it is desirable at all stages to maintain conditions of homogeneity and to reduce the period over which layers of widely different components are in contact.

Having obtained an effective ultimate dispersion in viscose, it is essential to maintain it during the whole of the process. Under the microscope dispersions prepared by the preferred method appear to be fully deflocculated immediately after preparation, but on standing they can slowly form floccules, indicating that what has been achieved is only a slowing down of the process (Fig. 4). Complete redispersion, nevertheless, is easily obtained by light mechanical action, and this would appear to provide the explanation of satisfactory practical usage. During passage through pipes, gear pumps, and even the filters themselves, constant shearing forces are operating, which, in the high-viscosity medium, are capable of mechanically preventing floccule formation.

Provided, therefore, that the particle size achieved in viscose is kept well below that which will pass the final filter, a tendency to flocculation under static conditions may have negligible effects on filtration behaviour. If the rate of flocculation were rapid enough to overcome the effect of normal shear occurring in the process, then filtration problems together with change in colour of the fibre would occur. The widespread successful use of pigments in the viscose process exemplifies the fact that the time factor in the behaviour of dispersions can allow non-stabilised suspensions to behave over the critical period of application as if they were stabilised.

B. PIGMENT PRINTING COMPOSITIONS

In contrast to viscose pigmentation, where the whole of the medium is either in solution or highly hydrated, the printing of textiles with pigmented compositions involves true emulsions of an aqueous phase and an essentially hydrophobic binder. Fundamental differences exist between the use of a dye and that of a pigment in this field. Whereas the former has a positive affinity for the fibre, and penetrates into it, the pigment is held mechanically on the fibre surface by a binder. Some of the wet fastness properties of dyes, e.g. to severe washing, therefore measure the degree to which the colouring matter can be resolubilised from within the fibre. When the same test is applied to a pigment-printed fabric, it tends to show little effect, provided that the binder is resistant to the reagent and to the weak mechanical action of the test. Binder systems which will completely resist a standard severe washing test, however, may show loss of colour when subjected to a hand washing test, where the greater physical action tends to break down the binder.

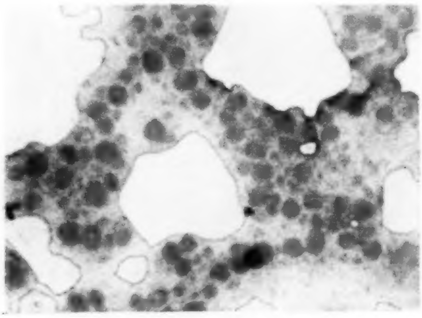
The principal problem in pigment printing has therefore been to obtain a binder which successfully binds the pigment to the fibre, giving fastness to wet and dry abrasion, and yet has the minimum effect on the handle of the fabric. Numerous systems are employed, but all are essentially based on emulsions which carry the pigment in the continuous phase. The practical usage of such pigmented compositions has already been described in the literature on this subject, and the basic dispersion requirements can be set down.

With the commonly used oil-in-water type of emulsion a typical system will consist of copolymer, e.g. of the vinyl–acrylic type, finely emulsified in a solution of a water-soluble cross-linking agent such as urea– or melamine–formaldehyde resin. Into the aqueous phase a high proportion of immiscible solvent such as white spirit is emulsified by the

FIG. 5— Cross-section of Phthalocyanine Blue Pigmented Textile-printing Composition on Filter-paper (× 300)

Dispersion obtained with non-ionic agent in the pigment paste (× 150)

FIG. 7A— P.V.A. Paint pigmented with Monolite Fast Yellow GNVS Paste (C.I. Pigment Yellow 1)



Dispersion obtained with non-ionic agent in the P.V.A. emulsion (× 150)

FIG. 7B— P.V.A. Paint pigmented with Monolite Fast Yellow GNVS Paste (C.I. Pigment Yellow 1)

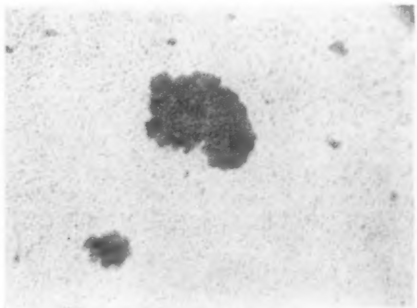


FIG. 8— Coagulation of Pigment in P.V.A. Paint on Storage (× 150)

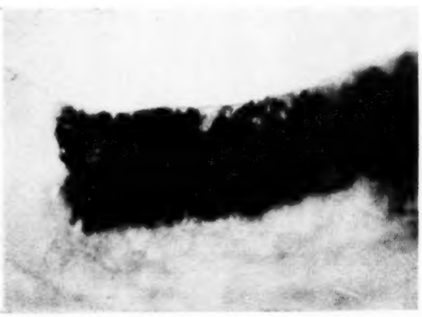
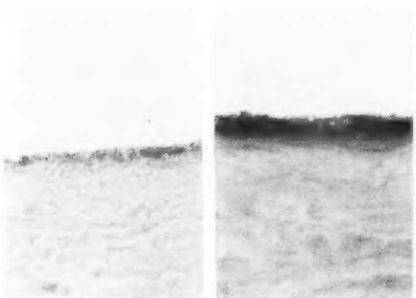


FIG. 10— Cross-section of Film showing Lump Formation resulting from Slow Addition of Pigment (× 300)



Monolite Red 4RHS (C.I. Pigment Red 7)

Monolite Fast Scarlet RNS (C.I. Pigment Red 3)

FIG. 13— Cross-sections of Ink Films on Paper (× 150)

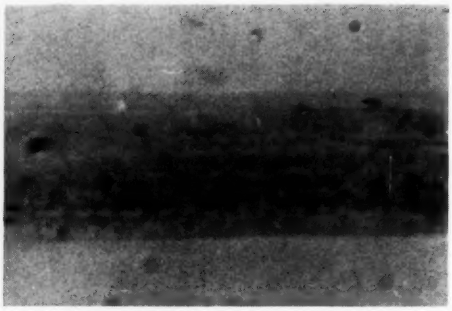
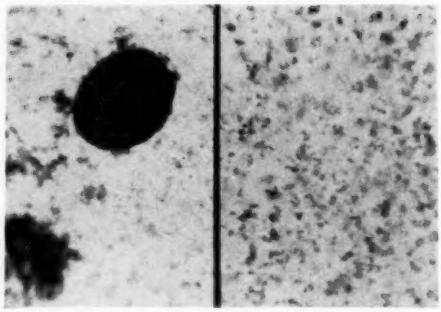


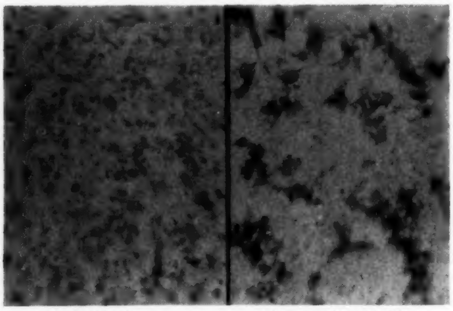
Fig. 1— Pigmented Viscose Filament (× 600)



Pigment paste added to viscose

Viscose added to pigment paste

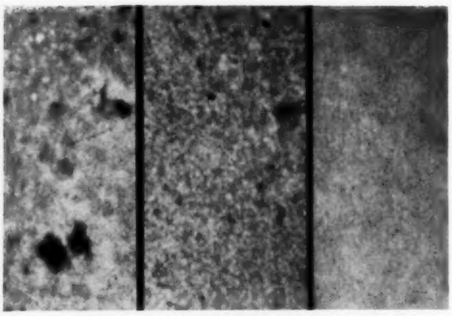
Fig. 3— Pigmented Viscose Solutions (×150)



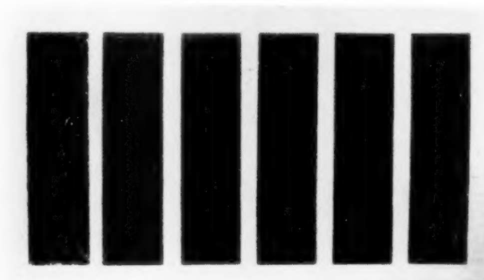
Immediately after preparation

After standing for 3 hr.

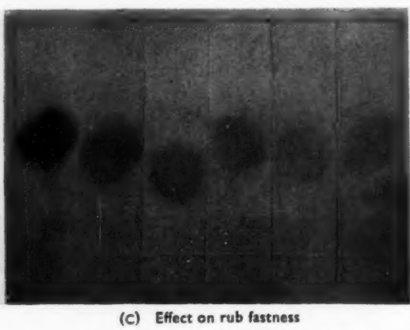
Fig. 4— Pigmented Viscose Solutions (× 150)



(A) Variation in degree of dispersion (× 150)

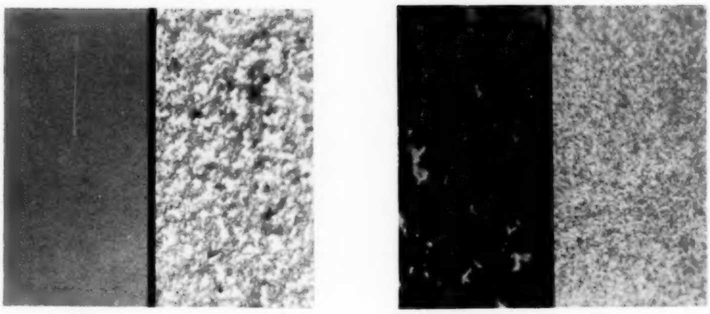


(B) Effect on hue and strength of prints



(C) Effect on rub fastness

Fig. 6— Textile-printing Compositions pigmented with Phthalocyanine Blue



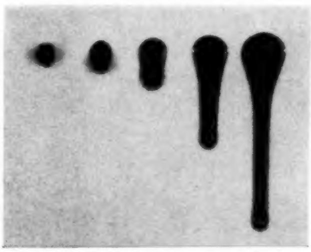
Dispersion in water (× 150) | Dispersion in oil (× 150)

(A) Prussian Blue treated with oxalic acid

Dispersion in water (× 150) | Dispersion in oil (× 150)

(B) Prussian Blue treated with sodium palmitate

FIG. 9



40 35 30 25 20

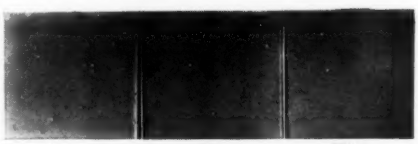
Pigment concentration (%)

FIG. 14—Critical Pigment Concentration for Flow under Gravity

Pure Middle Chrome GNS (normal) | Pure Middle Chrome LGS (treated)

FIG. 15—Litho Breakdown of Middle Chromes (C.I. Pigment Yellow 34)

Decreasing seeding →

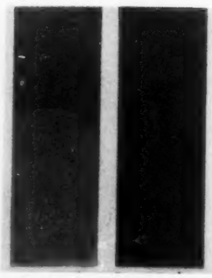


75% 60% 50%

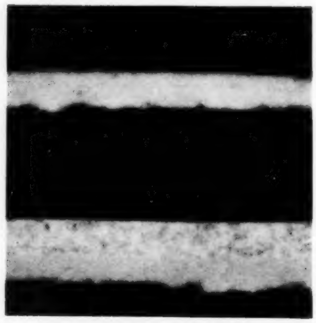
Resin concentration

FIG. 16—Variation in Seed Level with Concentration of Added Resin

FIG. 17— Phthalocyanine Blue Enamels dipped and sprayed



(A) Flocculation of Phthalocyanine Blue



(B) Cross-sections of Enamel Films (× 150)

FIG. 19

FIG. 20— Sedimentation Volumes of Phthalocyanine Blues

agent already present to provide the increased viscosity necessary for successful printing.

Particle size of the pigment must be fine, preferably in the region 0·1–1·0 μ., and this serves a dual purpose. Least effect on handle of the fabric can be achieved only by using the minimum of binder, so that maximum tinctorial strength is needed from the pigment. At the same time, particles need to be fully bound to the fibre to obtain good fastness to mechanical treatment, and the pigment should therefore penetrate with the aqueous phase into the finest interstices of the cloth and should not be filtered out on the surface.

Apart from any such filtration effect, pigment particles need to be small enough for the very thin binder film on individual fibre surfaces to hold them securely. The location of the pigmented film when a print is made on filter paper can be seen in Fig. 5. Dispersions have therefore to be prepared in a deflocculated or very weakly flocculated state to ensure penetration, and in practice each pigment requires individual consideration to obtain optimum stability in a particular system. Non-ionic surface-active agents have the advantage that they are less sensitive than other types of agent to electrolytes e.g. present as a catalyst.

On a strongly hydrophilic fabric such as a cellulosic cloth, deposition can be visualised as a penetration of the total system into the structure, with absorption of water by the fibres, and the rate at which this occurs will depend on the capillarity of the cloth structure, the effective viscosity of the system, and the surface tension of the continuous phase. Rapid take-up of water by the fibres renders them oil-repellent, and the resulting concentration of both the resin binder and the separately emulsified white spirit causes breakdown of these emulsions. At this stage, white spirit floods away from the systems by virtue of its low viscosity, but the much more highly viscous resin copolymer is held in the interstices of the cloth surface together with any excess of cross-linking agent in the water phase. Drying removes water and other volatiles, and subsequent baking cross-links resin to the fibre with the pigment remaining in the complex layer on the fibre surface. Such a process will result in pigment being fully bound, since it is, in effect, first deposited on the fibre surface and then bound by polymer, which accounts for the generally better rub fastness of oil-in-water as opposed to water-in-oil systems.

Taking a series of compositions, based on an oil-in-water system, the effect of varying the degree of dispersion of a phthalocyanine blue pigment can be illustrated (Fig. 6). When the degree of dispersion is poor, filtration leads to low penetration of the fabric, giving strong but dull effects together with difficulties in printing a uniform film. As fineness of dispersion is increased, better penetration results initially in brighter but weaker visual effects, with strength tending to increase as the ultimate tinctorial value of the fully dispersed pigment is approached. At the same time the greater penetration and more efficient binding which result from finer particles give rise to improved fastness to rubbing.

C. EMULSION PAINTS

Although some similarity of constitution exists between an oil-in-water textile-printing composition and an emulsion paint, the main problems encountered are quite different. The principal binders for emulsion paints have been based on styrene–butadiene, alkyd, polyvinyl acetate (P.V.A.), and acrylic emulsions, either separately or in mixtures, and in this country the polyvinyl acetate emulsions which have become most widely used have presented specific pigment dispersion problems. Whereas some of the other emulsions are normally stabilised by anionic agents and can therefore utilise similarly stabilised aqueous suspensions of pigments, such is not the case with P.V.A. emulsions. These commonly contain non-ionic agents, together with a proportion of polyvinyl alcohol acting as a protective colloid, and because the unplasticised emulsions give powdery films on drying, plasticisation is carried out during manufacture or during paint formulation with materials such as dibutyl phthalate. This promotes satisfactory film-forming properties in application and produces a softer, tougher film. In addition, it is necessary to add a colloid such as a water-soluble cellulose derivative or an etherified starch to act as a thickener for the aqueous phase and assist stability on storage.

The majority of paints contain also a dispersion of white pigment such as titanium dioxide to provide hiding power, and tinting is effected with aqueous dispersions of coloured pigments. Inorganic pigments present few difficulties, as they are essentially hydrophilic in nature, and in most cases can be deflocculated either by adsorbed inorganic ions, e.g. phosphates, or by anionic surface-active agents.

Difficult problems have, however, presented themselves in the use of organic pigments, concerning the state of dispersion of the pigment in the aqueous phase. In general, if it is essentially deflocculated at all times, then the pigment will not be prone to coagulation with particles of the binder. If, on the other hand, it is to any degree flocculated, then its consequently more hydrophobic surface can act as a nucleus for coagulation. It can do so by providing additional surface on which the non-ionic emulsion-stabilising agent can be adsorbed, thus lowering resistance of the polymer to coagulation. Then, with insufficient stability for both dispersions, the pigment and binder can coalesce. If the organic pigment dispersion is stabilised with anionic agent, sharing of the two agents can still occur, depending on the strengths of adsorption and concentration of non-ionic agent present in the pigmented emulsion. Deflocculation of pigment, therefore, does not necessarily mean that it will cause no breakdown of the emulsion, the stability of which depends on the concentration of its own type of emulsifying agent on the surface of the P.V.A. globules. A sufficient concentration is therefore needed to overcome the net force of attraction between polymer and pigment particles, and the use of non-ionic agents with organic pigments is now well established as a means of avoiding emulsion

breakdown. Certain pigments, notably azoic yellows based on acetoacetarylamides, show a strong tendency to coagulate all types of P.V.A. emulsion unless the pigment suspension is adequately stabilised. If this is, in fact, due to adsorption of surface-active agent required by the emulsion, then to avoid coagulation during addition of pigment paste, the concentration of non-ionic agent on the surface of emulsion particles must not be allowed to drop below that originally present. This effect can be demonstrated by controlled mixing of identical quantities of the same three components, but varying the mixing procedure. Where a non-ionic agent (Lissapol N) is added to the anion-stabilised paste (Monolite Fast Yellow GNVS, C.I. Pigment Yellow 1) before addition to the emulsion, no coagulation of emulsion occurs. When a non-ionic agent is added to the emulsion instead, the opposite is the case, and large agglomerates are built up, since the conditions necessary for coagulation exist over the whole period of addition (Fig. 7).

Such behaviour is seen to be of similar character to the effects obtained when dispersed pastes are mixed into viscose, and in each case, unsatisfactory dispersion results from diffusion processes occurring across the boundary between components before mechanical mixing has achieved homogeneity.

When P.V.A. paints tinted with similar yellow azoic pigments are stored for long periods, weakness with reddening and dulling of colour can occur, for which two explanations have been put forward. Of these, the common view has been based on flushing of pigment particles, i.e. transfer from aqueous to non-aqueous phase, but O'Neill[3] has shown that it can be associated also with severe pigment crystallisation. Both of these mechanisms can contribute to the technological effect in practice, depending on the composition of the total system. Azoic yellows are among the more strongly hydrophobic pigments, and even when substantially deflocculated with non-ionic agents will show weak flocculation behaviour in protective colloids. Conditions for emulsion particles of polymer and plasticiser to come into contact with pigment particles can therefore exist in the paint, which is a first requirement for crystallisation to occur. As a consequence, unless the pigment is completely stabilised in the aqueous phase, long periods of storage will allow time for an apparently stable paint to show the result of very slight instability. At the pigment concentrations used for paler depths, this is insufficient to cause any obvious emulsion breakdown. The effect can be illustrated by storage of an emulsion paint containing no opaque white, and coloured with a yellow dispersed azoic pigment (Monolite Fast Yellow GNVS). Loss in colour strength can be followed by using the paint at intervals during storage to tint a standard white paint, and examination of the final stored material shows evidence of agglomeration of pigment and polymer without affecting the bulk of the emulsion (Fig. 8).

Non-aqueous Systems

In the manufacture of most pigments, water has first to be removed before dispersion into non-aqueous media can be carried out. The great majority are therefore dried and pulverised, for in this form they provide the flexibility in use required by such major industries as paint and printing-ink manufacture.

For successful use of a pigment in dry powder form, its behaviour during incorporation, in combination with the efficiency of the mechanical process used, is of great importance. They determine how far the required degree of dispersion can be achieved, and can affect many of the application properties of the resultant pigmented system.

A. MIXING AND DISPERSION

At the start of its existence the technological properties of a pigment have been largely determined during precipitation by control of particle size and surface state. Drying and powdering conditions, however, can still exert marked modifying effects on the ease with which dispersion can be carried out. Most pigment filter cakes are in fact flocculated suspensions, and the consequent hydrophobic condition of the pigment surface facilitates release of water, while at the same time rigidity of structure helps to keep the filter cake in a porous condition, and to minimise blockage of the filter-cloth pores. At the drying stage, too, the hydrophobic condition of the pigment surface requires less work to remove water than would be needed for a more hydrophilic surface. The well known tendency for a deflocculated aqueous paste to dry to a dense, hard mass represents the effect that high adhesion tension has on water removal. Mechanical dispersion of treated Prussian Blue pigments into water and into a paraffin oil illustrates the generally complementary behaviour obtained. Treatment with oxalic acid gives a deflocculated suspension in water but a flocculated system in the oil, while treatment with sodium palmitate results in the opposite behaviour (Fig. 9). The majority of organic pigments, however, exist in a flocculated state in non-aqueous media, despite the broadly organophilic nature of their surfaces, and this is a clear indication of the virtual impossibility of completely stabilising non-aqueous suspensions of fine particle size.

Most of the common processes used for pigment dispersion involve no actual grinding, i.e. breakdown of primary particles, but instead there normally occurs a combination of wetting, separation, and partial deflocculation of particles. The majority of pigment powders contain a small proportion of agglomerates in which particles are more strongly bound than in the general bulk of the pigment. In both paint and printing-ink industries a major criterion of satisfactory dispersion is their effective elimination by milling or separation. Development of the optimum combination of tinctorial and flow properties will, however, depend largely on the degree and state of dispersion of the bulk of the pigment. Ideally, therefore, both conditions should be achieved simultaneously, but in practice this is seldom the case.

In a typical two-stage system, premixing of pigment and medium is followed by passage

through an efficient mill, e.g. of the three-roll type. Although at one time premixing was regarded simply as a means of eliminating gross air before milling, in recent years higher-powered mixers have been increasingly employed to do much of the work of dispersion. As a result, more complex and costly milling machinery has been used more economically to deal with coarser particles.

In using modern types of mixers, procedures are designed to make the pigment assist in its own dispersion. The low shearing action produced by oil medium alone is insufficient in many cases to achieve satisfactory dispersion, since there is no zone of intensive action. If, in the early stages of mixing, pigment powder is added gradually, superficially wetted pockets of pigment can be formed containing entrapped air. Low medium take-up by the pigment at this stage then tends to reduce the efficiency of wetting and dispersion of the subsequently added pigment, since unwetted particles are not contributing to the effective viscosity. The time factor is therefore extremely important, and studies have clearly shown the advantages of rapid addition of pigment in the case of titanium dioxide[4]. By this means, the effective viscosity of the mix is increased rapidly before any lumps have had time to form, and the resulting shear produced by higher initial pigment concentration breaks down powder agglomerates. This in turn accelerates the take-up of oil by the pigment surface and increases the effective dispersing action in the later stages of mixing. Despite their organophilic nature, organic pigments also can show formation of lumps when slow addition of pigment is made. This can be illustrated by slowly adding an azoic pigment (Monolite Red 4RHS, C.I. Pigment Red 7) to a mixer containing a medium-viscosity stand oil and examining a cross-section of a dried film prepared from the dispersion (Fig. 10). Particles which were discrete in the powder are seen to have adhered together in small lumps, between which relatively unpigmented medium exists.

By contrast, ball milling, one of the most common dispersion procedures in paint manufacture, is essentially a one-stage process. General requirements and conditions for efficient operation have been widely documented, and some specific data on changes in properties with time for certain pigments have been given by Fischer[5]. Essentially, the process depends on efficient cascading of the ball charge in the mill, and on all the pigment and medium coming under its action. The most interesting aspect which has come into prominence in recent years has been the use of suspensions of high pigment content to improve the efficiency of milling. This method utilises a titration procedure for determining the concentration of resin in solvent solution which will give a fluid mass with minimum addition to the pigment (Fig. 11). Resins can in this way behave as deflocculating agents, and the lower viscosity of medium normally involved provides more rapid initial penetration into the pores of the powder in wetting the pigment. Since milling is essentially by attrition between moving surfaces of the ball charge, which occurs efficiently only around points of contact, much of the suspension is moving through the larger interstices for most of the time. At the higher pigment concentration in the modified method, the pigment itself contributes more to the total milling effect, and a narrower particle-size range can be obtained. One of the difficulties arising from use of this method will be considered later.

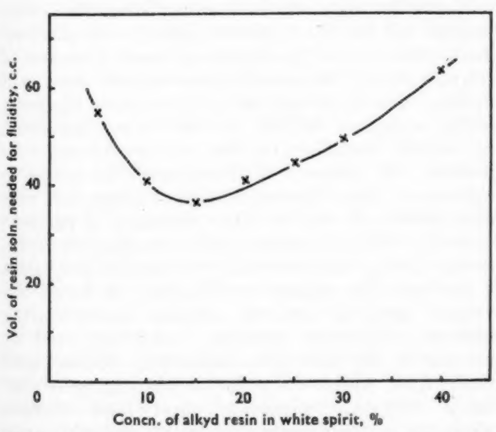


FIG. 11—Titration of Titanium Dioxide (C.I. Pigment White 6) with Alkyd Medium for Ball-milling

B. PRINTING INKS

Printing with oil-based inks involves the conversion of a mass of fluid suspension in bulk form to a large area of a very thin film. The order of conversion is indicated by the fact that 1,000 c.c. of ink at a film thickness of 1 μ. will cover 1,000 sq. metres. Of the many types of ink available, those printed by offset lithography can be considered most interesting from the dispersion point of view. Such an ink may be typified by a very fine dispersion of pigment at relatively high concentration in a heat-bodied drying-oil varnish, with other compounds present to control the precise behaviour of the ink at all stages of application. In simple terms, the lithographic process depends on printing from an ink-receptive image that is effectively coplanar with the non-printing area of the plate. The latter is maintained in a hydrophilic condition by application of a dilute aqueous solution, e.g. of an acid phosphate plus colloidal thickener, between each roller application of ink. Need to maintain a sharp image over long runs demands an extremely thin film of ink in the 0·5–2·0 μ. region, which must transfer under slight pressure from image to rubber-coated offset cylinder, and then to the paper, without distortion. This demands that all pigment particles should be held in the film of ink and should not transfer to any part of the aqueous system. Failure can occur by loss of particles too large to be held by the film, as these gradually build up on the offset cylinder, spoiling print quality. Alternatively, pigment can transfer into the aqueous phase by a reverse flushing process, causing deposition of colour in non-printing areas, or if small ink droplets emulsify into the aqueous system, a similar effect results. The dispersion properties

of the pigment in the ink are therefore of considerable importance.

Fineness of dispersion is controlled in practice by gauges, the use of which has been described in some detail by Walker and Zettlemoyer [6]. Two properties are assessed, corresponding to the separable particle-size characteristics considered earlier. In testing, a sample of ink is forced by a scraper into a long wedge-shaped channel accurately cut into a steel block and varying in depth from zero to 0·001 in. The general fineness is then judged by overall interference with gloss of the ink and by the upper limit of occasional coarse particles which show up as scratches. Although an ink would normally be rejected on a basis of, say, 10 scratches above the 5 μ. depth, the proportion of pigment responsible would be only of the order of 1 p.p.m., and a severe criterion is therefore applied.

During milling to reduce coarse particles below the critical size, the remainder of the pigment is undergoing similar treatment. For example, it has been shown by Holtzmann [7] that organic pigments such as Benzidine Yellows and Lithol Reds exhibit definite changes in properties with change in mean particle size. In general, decrease in size, in addition to improving fineness of grind rating, improves colour value and gives less fluid inks. The higher proportion of extremely fine particles which can be obtained while milling to reduce coarse particles will result in a greater degree of flocculated structure in the ink. Such a change, however, is not always accompanied by extra colour value, which tends in practice to reach a maximum as milling proceeds. By dispersing a pigment of fine ultimate particle size (Monolite Fast Bordeaux 2RS, C.I. Pigment Red 12) to various levels of fineness, this point can be illustrated (Fig. 12). Tinctorial strength, as measured by the quantity of ink per unit area required to give a standard depth of colour, rapidly reaches a maximum at low milling efficiency. Relative gloss

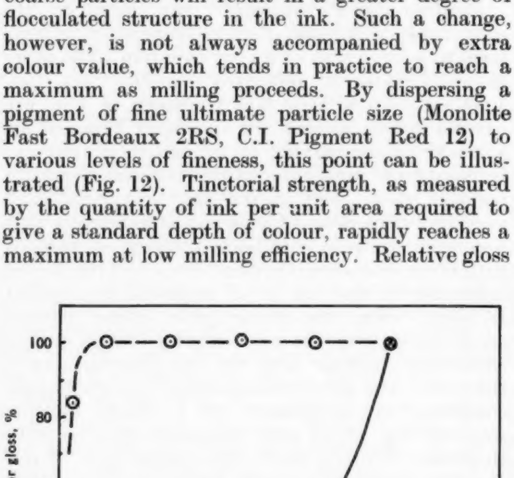


FIG. 12— Effect of Dispersion on Strength and Gloss: Monolite Fast Bordeaux 2RS (C.I. Pigment Red 12)

of the printed ink, however, rises with increased efficiency, indicating the higher degree of flocculation.

Both the degree and the state of dispersion in an ink can considerably affect distribution properties on the printing press, and subsequent behaviour in relation to paper. As Coupe and Smith [8] have shown with Carbon Black inks, paper having extremely fine interstices gives the greatest penetration of medium as a result of high capillarity, and low penetration of pigment owing to filtration. The rate and the degree of pigment flocculation over the period following contact of ink and paper will, therefore, determine the magnitude of the opposing force tending to hold medium in the ink film. This can be demonstrated by comparison of equivalent ink films on paper, prepared from inks of equal pigment volume concentration (15%) in a standard lithographic varnish medium. Whereas a more highly flocculated organic pigment (Monolite Red 4RHS) produces glossy prints of good rub resistance, a pigment with lower capacity for structure formation (Monolite Fast Scarlet RNS, C.I. Pigment Red 3) gives a matt surface, inadequately bound owing to loss of medium into the paper (Fig. 13). Such differences can in fact be related to the ultimate ability of the pigment to extend its flocculated structure in the medium.

By gradual dilution of a normally milled ink with additional medium, the pigment concentration can be determined at which flow under gravity of the rested ink starts to occur (Fig. 14). For the two pigments considered above, the respective concentrations are approx. 8·5% and 22% by volume. Such figures clearly indicate the appreciably higher degree of anisometry of units in the flocculated structure of Monolite Red 4RHS. Differences between pigments can therefore be interpreted on the basis of flocculation into rod-like units forming a three-dimensional structure, and the ability of a pigment to maintain this structure as dilution increases will be, in effect, a measure of the number of particles in an average rod-unit.

Unsatisfactory printing, resulting from the tendency for pigment to transfer from the lithographic ink to the aqueous phase, is dependent also on the state of particle dispersion. Transfer of this nature may be related to the reverse process of flushing, where an aqueous suspension of pigment, having a greater affinity for the oil medium than for water, transfers to the oil on mixing. In practice, the degree of flocculation in water is important, since it determines in combination with other factors the rate and the efficiency of pigment transfer. With fundamentally hydrophilic pigments, such as lead chromes, the surface properties of the particles require modification to avoid the reverse flushing process taking place during printing. Aqueous fountain solutions used in practice on the litho press frequently contain acid phosphates, which act as deflocculating agents for many inorganic pigments, and lead chrome pigments in their normal state therefore have a strong tendency to phase transfer during printing.

If, however, their surfaces have been modified so that stronger adsorption of components of the media, e.g. fatty acid groups, occurs, better transfer resistance can be obtained. The relation of this effect to normal flushing can be illustrated by flushing aqueous pastes of treated and untreated middle chrome pigments into the same lithographic varnish, where, although both pigments flush, the former shows more rapid transfer. After complete drying, the resulting inks show a marked difference in resistance to breakdown in fountain solution, as indicated by the coloration obtained under standard test conditions (Fig. 15). Despite the fact that it transfers into the varnish during flushing, therefore, the untreated chrome retransfers into the phosphate-containing fountain solution. Such behaviour indicates that, while the adsorbed varnish component is capable of displacing water from the untreated pigment surface, the more strongly adsorbed phosphate can in turn displace the varnish component.

C. PAINTS

In the earlier consideration of ball milling using high-pigment–low-resin systems, the advantages in efficiency were noted, but problems can arise in the subsequent dilution of the dispersion obtained. Normally, a resin solution of substantially higher concentration is to be added to the ball-milled suspension, in order to bring the pigment: binder ratio to the correct practical level, and during mixing small lumps or "seeds" can be formed which will not disappear under normal agitation conditions.

The effect has been studied by Daniel [9] for a system based on titanium dioxide pigment in an alkyd resin medium, and he has demonstrated that, at a static boundary between mill-base and concentrated resin solution, there is clear evidence of loss of liquid by the mill-base. Such behaviour may be explained on the basis of rapid diffusion of the lower-molecular-weight solvent from mill-base to resin solution, due to the differential resin concentration at the boundary. In practice this will result in a reduction in volume of the mill-base, and a resulting higher pigment concentration, providing increased resistance to the action of the mixer. As in the examples of mixing dispersed pigment pastes into viscose or P.V.A. emulsion, the present effect is largely dependent on the time factor, and slowing down the rate of solvent diffusion can materially affect the result. For this reason, if the concentration of resin in the mill-base and the added solution are brought closer together, seeding can be decreased. Ball-milling a scarlet chrome (Pure Scarlet Chrome YS, C.I. Pigment Red 104) at high pigment content into a medium-oil-length alkyd-resin solution in xylene can be used to demonstrate this effect (Fig. 16). Dilution of the mill-base, which contains a 20% resin solution, with solutions of higher concentration shows appreciable "seeding" with added 75% resin solution, the effect decreasing as the concentration approaches that in the mill-base. In practice such a procedure would not always allow the correct final composition to be achieved, and the resin concentration used in milling also would need to be raised.

With certain pigments, notably phthalocyanine blue, the degree of flocculation in paint media is particularly high. Use of this pigment in combination with titanium dioxide can show an appreciable apparent loss of tinctorial strength when applied as a paint film. Although the mechanism is not fully understood, the practical problems which arise are frequently the direct result of non-uniform conditions in formation of the film. For example, the same alkyd/urea–formaldehyde stoving enamel applied by dipping and also by spraying gives a markedly higher colour strength by the latter method. In the dipping process mechanical action during application is negligible, and solvent evaporation relatively slow, both conditions tending to allow flocculation to occur. Spraying, on the other hand, produces high turbulence in the jet, and solvent loss from the film is rapid, giving least mobility and least time for particles to associate. It can be observed that the effect of increasing ratio of blue: white pigment is to reduce the contrast obtained between sprayed and dipped areas (Fig. 17). This suggests that the flocculated blue pigment (Monastral Fast Blue LBXS, C.I. Pigment Blue 15) is acting as a uniform system at higher concentrations, and gloss measurements confirm the anticipated effect on the dipped paint film surface (Fig. 18). At low ratios of blue: white pigment, clear separation of blue floccules occurs in a film applied by dipping, as can be seen in a cross-section (Fig. 19A).

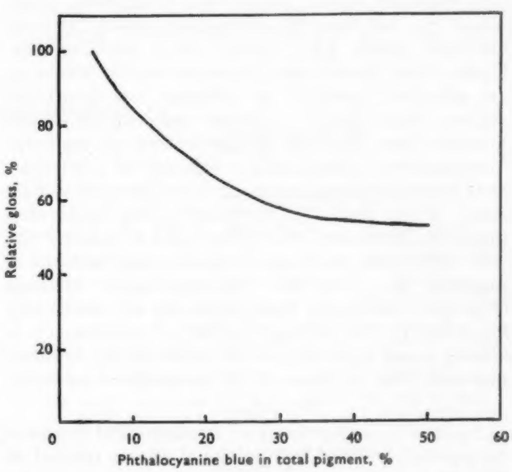


FIG. 18—Effect of Flocculation on the Gloss of a Stoving Enamel: Monastral Fast Blue LBXS (C.I. Pigment Blue 15)

In decorative paint systems which have higher application viscosity, and contain solvents causing less flocculation, the effect is considerably reduced, and normally will occur only on faulty application, such as runs and sags due to films of abnormal thickness being applied.

To overcome this general defect, considerable work has been carried out with the object of modifying phthalocyanine blue so that it flocculates

to a far lower degree. Treatment of the pigment with various derivatives of copper phthalocyanine has constituted the principal approach, in an effort to find a deflocculating agent which would be adsorbed on the particle surface. Varying success has been achieved with certain metal phthalocyanines, sulphonated phthalocyanines, and other more complex derivatives. The specific behaviour of the resulting modified pigments in different types of paint media varies so much that no single treatment devised solves the problem in all media. Nevertheless, correlation between the technological effect and the particle behaviour can be confirmed by comparing cross-sections with the visual effect obtained by dipping and spraying stoving enamels prepared from both flocculation-resistant and unmodified pigment (Fig. 19B).

Although attempts have been made to explain the fundamental action of compounds devised for surface treatment, no clear evidence has yet been presented. From recent work, Lacey, Roberts, and Giambialvo have concluded that the action of some of the specialised derivatives of copper phthalocyanine is not due solely to the reduction of the high surface energy of the copper phthalocyanine particles[10]. In systems containing polar solvents, they describe the stabilisation of floccule size to roughly 1 μ. as compared with a calculated ultimate particle size of the order of 0·05 μ. These phthalocyanine derivatives are therefore considered to act by amphipathic adsorption, with the substituent groups highly solvated by solvent present in the medium.

A general mechanism of this kind for partial deflocculation would involve an equilibrium state where no net force of attraction exists between floccules which have grown to a limiting size. Under these conditions a floccule would behave as an effective particle, in absence of disruptive action, but should contain substantially less medium than floccules of the untreated pigment. Comparative sedimentation volumes of a flocculation-resistant phthalocyanine blue (Monastral Fast Blue RFS) and the corresponding untreated pigment (Monastral Fast Blue LBXS) confirm the wide difference existing at equal concentrations of pigment in a diluted stoving-enamel medium (Fig. 20). Although both pigments are essentially flocculated, the average degree of anisometry is clearly much lower in unit floccules of the modified pigment than in those of the unmodified material.

* * *

Against a background of fundamental pigment properties, selected technological effects related to pigment dispersion have been discussed. Consideration of the separate aspects has shown the broad pattern of dispersion behaviour existing in both aqueous and non-aqueous media.

We find that a high degree of dispersion, in addition to providing tinctorial strength, ensures adequate binding in thin films and permits the use of a pigment in processes where its separation by filtration is undesirable.

With mixing operations involving predispersed pigments, we may conclude that any differences between the components forming a temporary boundary need to be minimised if good dispersion is to be maintained. Similarly, in mixing or milling powders into liquids, both the rate of addition and the pigment concentration can affect significantly the efficiency of the operation.

In the final pigment suspension, flocculation characteristics determine many important application properties of the system. Among these are its flow behaviour, including its ability to retain medium, and those tinctorial differences resulting from alternative methods of film application.

The significance of the time factor also is apparent, particularly where a mechanically deflocculated suspension is found to behave as if it were essentially stabilised.

Future progress in the many fields of application for pigments will, I believe, depend largely on the extent to which we can control their degree and state of dispersion at all stages of use.

In conclusion, I would like to thank those of my colleagues who have assisted in the preparation of this paper and its accompanying illustrations.

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New Ideas in the Application of Phthalocyanine Derivatives to Textiles

F. GUND

Meeting of the West Riding Section held in the Griffin Hotel, Leeds, on 12th February 1959, Mr. R. Heaton in the chair

Practical experience with the monomeric diiminoisoindoline and the metal–polyisoindolines is described, and the differences between Phthalogen dyes of these two types are discussed in connection with their dyeing characteristics and their methods of application. New Phthalogen products based on a monomeric compound of analogous structure to the diiminoisoindoline, but containing an additional heterocyclic ring, are described. An outline is given of the properties of the azoic coupling component, Naphthol AS–FGGR, which is a phthalocyanine derivative.

INTRODUCTION

Since the author's previous lecture was published [1], a number of important papers regarding phthalocyanine derivatives have appeared, mainly in connection with application techniques [2–5]. The object of the present paper is to describe further experience which has been gained with dyes of the phthalocyanine class manufactured and developed by the Farbenfabriken Bayer. Previous information about these dyes is supplemented, and a description is given of the properties and application of new compounds of the same class.

The characteristics of the Phthalogen dyes which have been in use for some time are summarised in Table I.

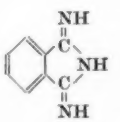
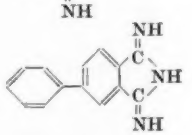
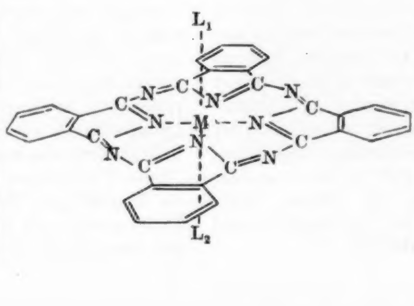
The Diiminoisoindolines

The diiminoisoindolines (aminoiminopseudoisoindoles), Phthalogen Brilliant Blue IF3G (C.I. Ingrain Blue 2) and Phthalogen Brilliant Green IFFB, are the respective monomeric primary products in the production of phthalocyanine and of tetraphenylphthalocyanine. Some time ago Phthalogen Brilliant Blue IF3GM made its appearance on the market. This is a physical mixture of the monomeric primary product and an organic copper-complex compound, Phthalogen K [1]. Recently an organic nickel complex of similar composition was marketed as Phthalogen NI, and a physical mixture of this complex and the monomeric primary product was marketed as Phthalogen Turquoise IFBM. The two mixtures, Phthalogen Brilliant Blue IF3GM and Phthalogen Turquoise IFBM, produce the same results as those obtained by using Phthalogen Brilliant Blue IF3G with Phthalogen K and Phthalogen NI, respectively. Use of the nickel complex yields somewhat brighter hues than can be obtained when a nickel salt is used to produce the turquoise colour, either by dyeing or printing.

With Phthalogen Turquoise IFBM, in direct printing, a mixture containing a high proportion of the cheaper Levasol F (formamide), as well as Levasol P or PO, can be used. For example, in a paste containing, per kg., 30 g. Phthalogen Turquoise IFBM, 20 g. Levasol PO and about

TABLE I

Survey of Phthalogen Dyes

Chemical Character	Designation	Formula	Auxiliaries (Solvents) used in Application	
Monoisoindoline derivatives	Phthalogen Brilliant Blue IF3G (metal-free)		Phthalogen K and NI Levasol P, PO, F, TR Emulsifier W	Low mol.wt. Soluble in water and in water-miscible solvents Highly diffusing Limited stability due to hydrolysis Reactivity with amines (suitability for resist-printed grounds) Reactivity with formaldehyde (not applicable with vat dyes)
	Phthalogen Brilliant Green IFFB (metal-free)		Phthalogen K Levasol P, PO, F, TR Emulsifier W	
	Phthalogen Brilliant Blue IF3GM (metal-containing)	Physical mixtures of IF3G and a copper and a nickel complex, respectively	Levasol P, PO, F, TR Emulsifier W	
	Phthalogen Turquoise IFBM (metal-containing)		Levasol P, PO, F, TR Emulsifier W	
Metal-polyisoindolines	Phthalogen Brilliant Blue IF3GK L_1 = Isoindoline component L_2 = Alkylol M = Copper		Levasol ND, DG	High mol.wt. Insoluble in water, soluble in solvents Good stability, no hydrolysis No reactivity with amines (cannot be resisted, applicable with Aniline Black)
	Phthalogen Turquoise IFBK L_1 = Isoindoline component L_2 = Alkylol M = Nickel		Levasol ND, DG	
	Phthalogen Blue IB L_1 = Isoindoline component L_2 = $H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ M = Cobalt		Levasol R (reducing agent)	Insensitive to formaldehyde (applicable with vat dyes) Transformation into phthalocyanine by reduction (can be used on Naphthol prepare without steaming)

95 g. Levasol F are sufficient, whilst with 30 g. Phthalogen Brilliant Blue IF3GM the amounts are 75 g. Levasol PO and 40 g. Levasol F.

PRACTICAL CONSIDERATIONS

Of the diiminoisoindolines, the cheaper Phthalogen Brilliant Blue IF3G (or IF3GM) has been adopted in a wide field of application, whereas Phthalogen Brilliant Green IFFB is of less importance as far as quantity of dye is concerned. The reason is primarily the high cost of the Green, for both printing and dyeing, as well as the fact that although it is slightly brighter than vat dyes of similar hue, it does not provide such a popular fashion shade as the unique clear blue of the pure phthalocyanine. However, Phthalogen Brilliant Green IFFB has attained considerable importance as a shading dye for the turquoise blues which are still so much in demand.

The natural field of application for Phthalogen Brilliant Blues IF3G and IF3GM, Phthalogen Turquoise IFBM and Phthalogen Brilliant Green IFFB is in pad dyeing or for resist styles. The quantities mainly used for blue and turquoise shades with the Brilliant Blues and the Turquoise are 0·5–1·0% on the weight of material. All types of cloth, e.g. mercerised cottons, poplins, and heavier fabrics such as twills and corduroy, are dyed by the padding method. Where turquoise shades of optimum brightness and fastness are required, mixtures of about equal parts of Phthalogen Brilliant Green IFFB and Phthalogen Brilliant Blue IF3G are suitable, using the quantities indicated above.

Resist styles illustrate the special position occupied by the monomeric diiminoisoindolines. By simple and comparatively inexpensive means it is possible to obtain results which are notable for their sharp outlines, plastic effect and purity of colour. In the United States a method has been adopted in which the goods are first printed with resists, dried and steamed, and then slop padded in the same way as for solid-shade piece dyeing. After drying, the goods are developed by dry heat, e.g. by treatment at 350°F. for 90 sec.

As described elsewhere [6], it is also possible to use zinc salt resists, which probably form a readily cleavable zinc complex which can be removed by washing during the aftertreatment. Resists with Phthalotrop B, however, are still used extensively, but it is important to adjust the concentration of the resist to the concentration of the padding liquor.

The results obtained also depend upon mechanical conditions such as type of engraving, pressure during printing and the squeezing effect during padding. Either nip padding or slop padding may be employed. Coloured resists are produced mainly with dyes of the Rapidogen type or with pigments. The latter are applied either as oil-in-water or as water-in-oil emulsions. Aniline Black can be used, as development of the black by the intermediate steaming has already been completed before padding, so reaction between aniline and diiminoisoindolines can no longer take place. Rapidogens are used for full depths, and pigments for medium-to-pale depths.

The method recommended originally consists of printing the resists, drying (but not steaming), padding, and then developing the resist colours and the ground in a single steaming passage. This has proved suitable to some extent, particularly with the deeper blue grounds. Levasol PO must be used in the padding liquor if the phthalocyanine is to be developed by steaming.

STABILITY OF THE DIIMINOISOINDOLINES

One well known disadvantage of the monomeric diiminoisoindolines is their tendency to hydrolyse, so the stability of aqueous solutions and printing pastes is limited. In practice this poor stability causes less trouble in pad dyeing than in printing. A fairly large volume of the solution, required for large batches, can be kept satisfactorily at a low temperature, or if necessary, a new mixture can be prepared after 3–4 hr.

Fig. 1 shows the loss of reactable diiminoisoindoline which occurs after standing for periods of up to 24 hr. at 0–50°C. The pad liquor consisted of—

20	Phthalogen Brilliant Blue IF3GM
20	Methanol
20	Emulsifier W
30	Levasol TR
70	Urea
840	Water
1000	

It is seen that stability can be increased considerably by reducing the temperature, so it is advisable to keep solutions which are not intended for immediate use in a refrigerator or a cold-storage room.

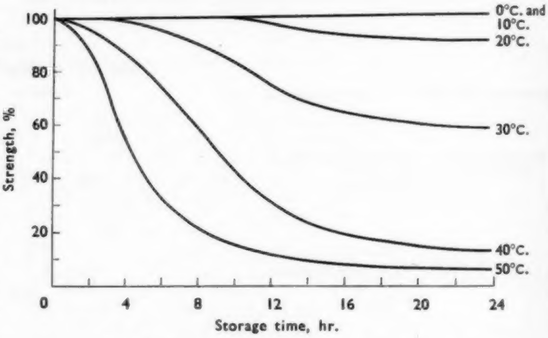
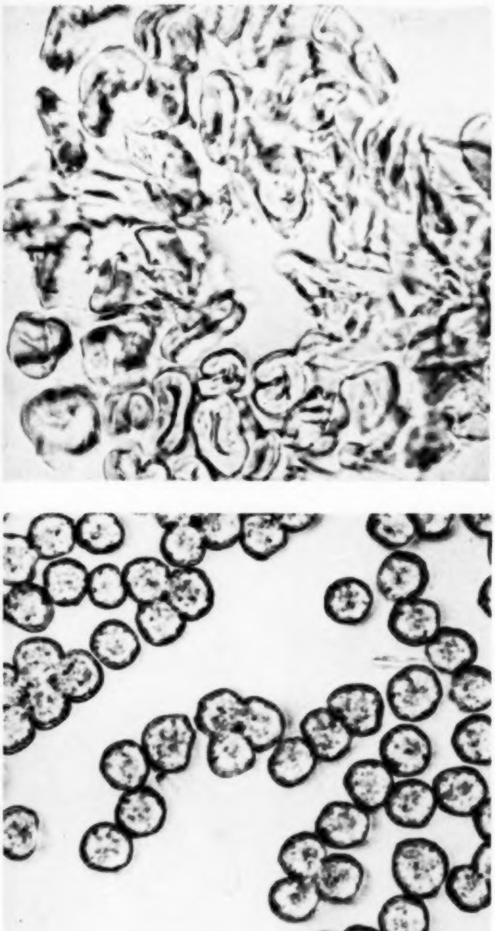


FIG. 1—Loss of Diiminoisoindoline on Storage

The Metal–polyisoindolines

The monomeric isoindolines possess good solubility, but show a tendency to hydrolyse and to react with amines and aldehydes, which is one reason why they cannot be printed alongside vat dyes without taking special precautions. The metal–polyisoindolines, on the other hand, do not possess these disadvantages; whilst giving colours of equal clarity and brilliance, they can be used in fields which are barred to the monomeric products. These Phthalogen complexes, which are marketed as Phthalogen Brilliant Blue IF3GK (formerly IF2G conc.) and Phthalogen Turquoise IFBK, give printing pastes of much better stability, and can be

Phthalogen Brilliant Blue IF3GK (Metal–polyisoindoline)



(A) Cotton
(B) Continuous-filament Cuprammonium Rayon
(C) Spun Viscose Rayon

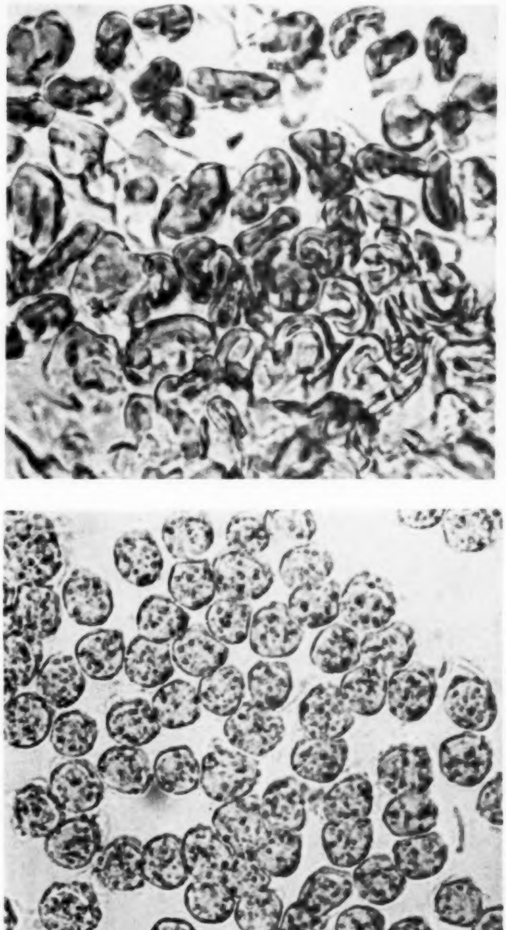
Fig. 2— Fibre Cross-sections: Paddings at 20°c.

Phthalogen Brilliant Blue IF3GM (Diiminoisoindoline)

(A)

(B)

(C)



(A) Cotton
(B) Continuous-filament Cuprammonium Rayon
(C) Spun Viscose Rayon

Fig. 3— Fibre Cross-sections: Paddings at 20°c.

Phthalogen Brilliant Blue IF3GK (Metal-polyisoindoline)

Cotton

Viscose Rayon

Continuous-filament Cuprammonium Rayon

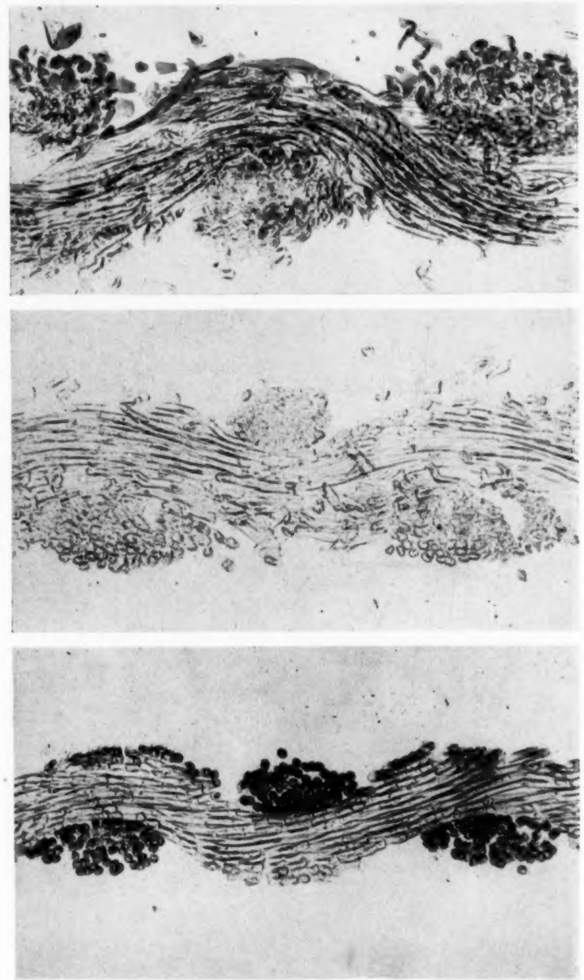


FIG. 4— Sections through Prints

Phthalogen Brilliant Blue IF3GM (Diiminoisoindoline)

Cotton

Viscose Rayon

Continuous-filament Cuprammonium Rayon

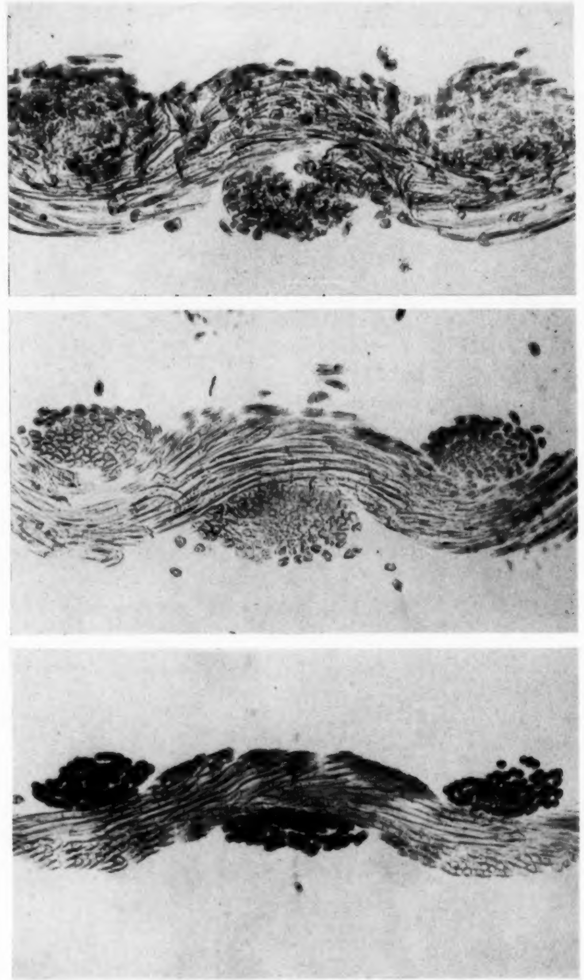


FIG. 5— Sections through Prints

FIG. 4— Sections through Prints

FIG. 5— Sections through Prints

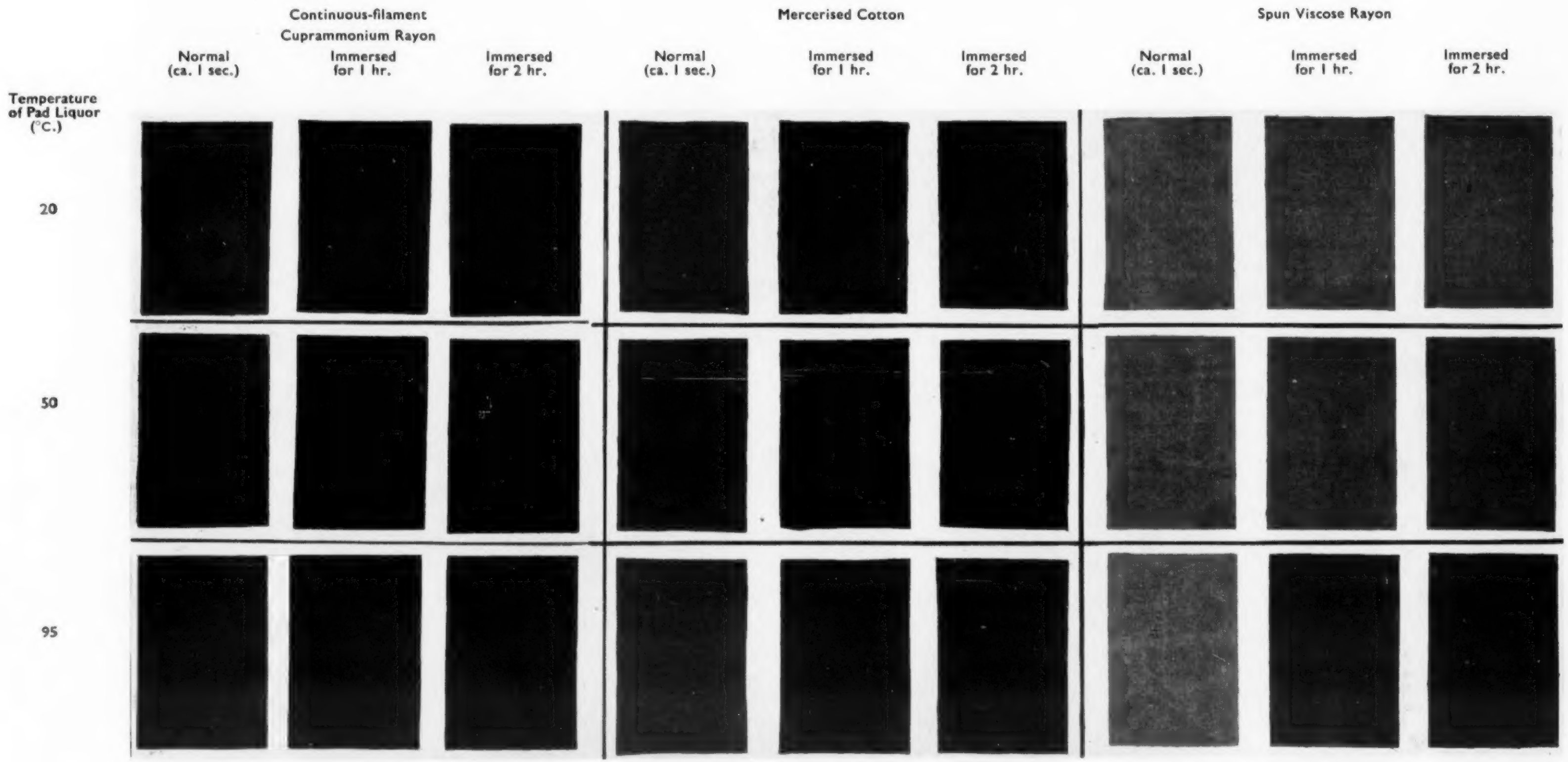
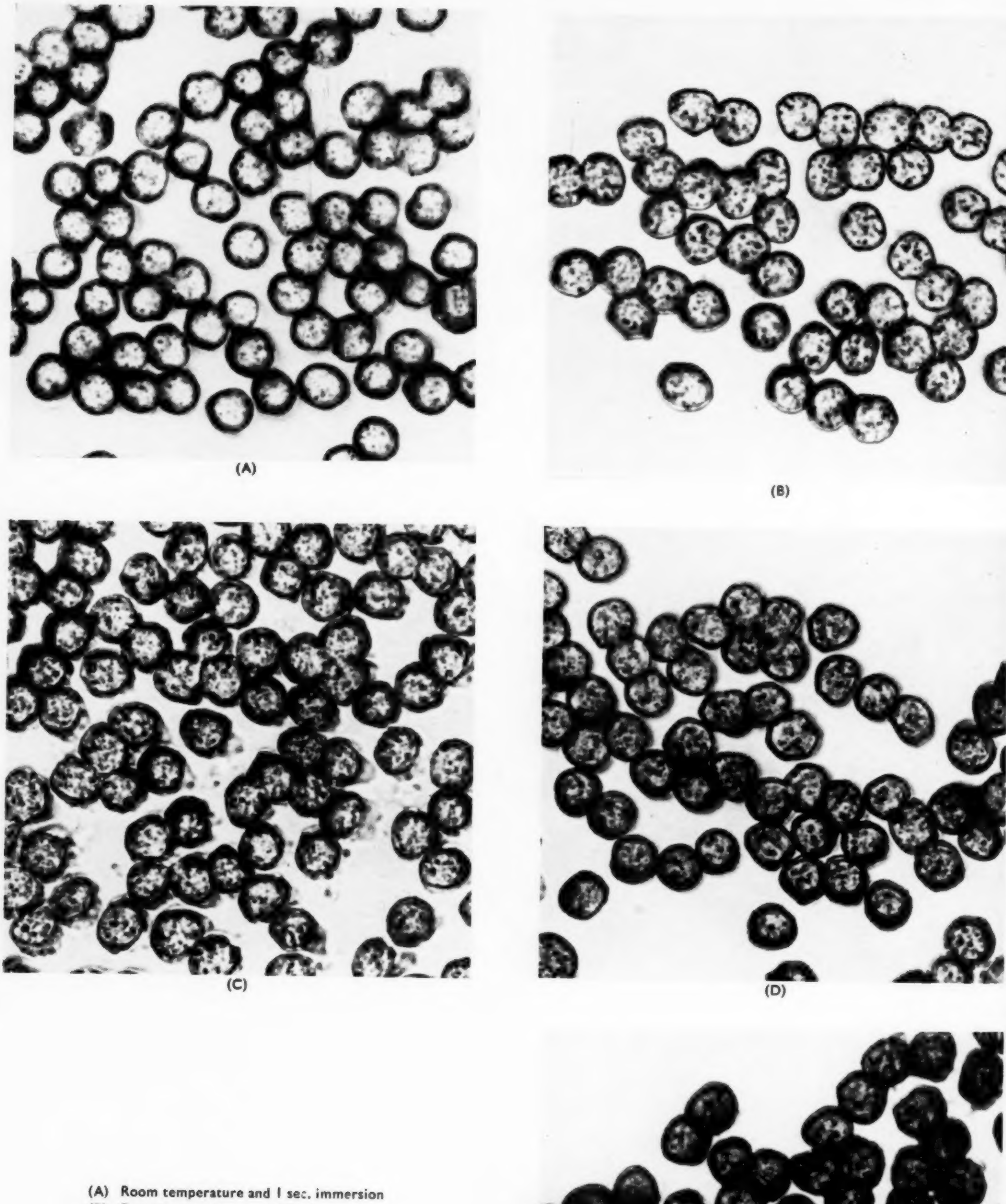


FIG. 7— Naphthol AS-FGGR → Fast Red Salt TR



(A) Room temperature and 1 sec. immersion
(B) Room temperature and 2 hr. immersion
(C) 50°C. and 1 sec. immersion
(D) 50°C. and 1 hr. immersion
(E) 95°C. and 1 hr. immersion

(All paddings were dried and developed with Fast Red Salt TR)

FIG. 8— Cross-sections of Cuprammonium Rayon padded with 20 g./litre Naphthol AS–FGGR

printed alongside vat dyes and Aniline Black. They possess a similar chemical basis and differ only in the metal (in one case copper, in the other case nickel), whereas the cobalt–polyisoindoline complex, Phthalogen Blue IB, occupies a special position owing to its basic character and the fact that it is applied from an acid medium. Its solubility in acid makes it possible to omit the solvent (Levasol ND), although it is necessary to use a special reducing agent marketed as Levasol R. Phthalogen Blue IB also is unaffected when steaming alongside vat dyes. All three metal–polyisoindolines can be developed with steam in the usual manner. Phthalogen Brilliant Blue IF3GK and Phthalogen Turquoise IFBK are insoluble in water, so a solvent mixture, Levasol ND, is used to dissolve the dye when preparing the printing paste. When the dye solution is stirred into the printing paste the dye is precipitated as a fine dispersion. As soon as the water has evaporated from the printed paste, the precipitated dye redissolves in the solvent and penetrates into the fibre. Both dyes can also be converted into phthalocyanine after the drying operation by dry-heat treatment.

WET DEVELOPMENT OF THE PHTHALOGEN COMPLEXES

All three metal–polyisoindolines can be converted into phthalocyanine by the application of reducing agents in aqueous solution. Either sodium bisulphite or alkaline hydrosulphite solutions are suitable for this type of wet development. The former is used if the Phthalogen complex is printed on a naphtholated ground alongside azoic diazo components. After drying, the goods are passed through hot bisulphite solution in order to develop the phthalocyanine.

Development with alkaline hydrosulphite or Rongalite–potash solution is suitable when printing Phthalogen complexes alongside vat dyes by the two-phase printing process (Colloresin process and "flash" process). The dyes are very suitable for direct printing alongside vat dyes by the Colloresin process, and in "fall-on" styles both vat and Phthalogen dyes can be developed satisfactorily. The procedure is to print the dyes in the usual way, dry, and then pad with a solution of either Rongalite–potash or hydrosulphite–caustic soda, finishing with a steaming operation of the necessary duration.

FURTHER POSSIBILITIES IN TEXTILE PRINTING

Phthalogen Brilliant Blue IF3GK and Turquoise IFBK can also be applied in overprinted designs by printing alongside vat dyes by the potash–Rongalite method. When printing alongside vat dyes, however, the reducing effect of the Rongalite should be borne in mind. A suitable sequence for the printing rollers— which is made possible by including crush rollers— is arranged to prevent contamination of the Phthalogen paste by the vat paste. Bisulphite induces almost immediate reduction and conversion to phthalocyanine, whereas potassium sulphite can remain in the printing pastes containing Levasol ND without having any immediate reducing action, thus enabling the dyes to be used for resist effects under Variamine Blue pad-dyeings.

Phthalogen complexes are also suitable for resists under Aniline Black, zinc oxide and triethanolamine being used as resisting agents.

PENETRATION DURING DYEING AND PRINTING

In comparison with the diiminoisoindolines, the metal–polyisoindolines have much higher mol.wt. and so cannot penetrate easily into the cellulosic fibre. Fibre cross-sections show good penetration by the monomeric isoindolines, whereas only ring-dyeing is obtained with the polyisoindolines, the inner part of the fibres remaining practically colourless (Fig. 2–5). Owing to their low rate of diffusion, the metal–polyisoindolines are not suitable for viscose rayon.

DYEING WITH METAL–POLYISOINDOLINES

Padding

Pale-to-medium depths of good fastness can be obtained by pad dyeing with Phthalogen Brilliant Blue IF3GK and Phthalogen Turquoise IFBK in conjunction with Levasol ND. The cost of using this solvent is relatively high, since at least 200 g./litre must be used, regardless of dye concentration. Recently a formula using Cellosolve and Emulsifier W as solvents has proved very suitable for depths up to 0·5% Phthalogen Brilliant Blue IF3GK, as well as being more economical than the use of Levasol ND, since less solvent is needed. Wet development of the padded and dried goods with sodium bisulphite at 90°C. is preferable in this case.

Dyeing in a Long Liquor

A method of application has been discovered for the metal–polyisoindolines which enables them to be used in a long liquor. As shown by Baumann *et al.*[4], Cu^{++}–polyisoindolines have good solubility in glacial acetic acid, but are not stable in this solution and gradually hydrolyse. This excellent solubility in glacial acetic acid can be utilised, with simultaneous suppression of hydrolytic degradation, if a mixture of glacial acetic acid and diethylene glycol is used. (Phthalogen Turquoise IFBK requires a mixture of glacial acetic acid, formic acid and diethylene glycol.) The highly concentrated solutions obtained give clear dyebaths on dilution, and these possess sufficient stability for use at room temperature. Owing to the high solubility of the dyes the quantity of solvents required is not excessive. Presumably, the solubility in glacial acetic acid is due to the cationic nature of the metal–polyisoindolines. The diethylene glycol also appears to play a part, since the solution is not immediately ready for use, but has to stand for 15–20 min. before dilution. It is important to keep moisture away from the solution during preparation: aqueous acetic acid is not suitable. Concentrated solutions should be used as soon as possible, and splashes of water into the mixture should be avoided. After diluting the concentrated solution with water, its stability is poor and dyeing should be started immediately.

From the diluted solution in acetic acid, the metal complex quickly exhausts on to the cellulosic fibres, which have previously been treated with anionic compounds. Suitable mordants include tannin–tartar emetic and the Katanols, although clearer and faster dyeings have been obtained by using sulphonated aromatic compounds possessing substantivity, e.g. *Phthalofix FN*. Mordanting is carried out by adding dissolved Phthalofix FN to the hot neutral liquor, treating the material for a time in the hot liquor, then adding Glauber's salt in portions and continuing treatment for 20 min.; this is followed by rinsing with a salt solution to cool down the material. The mordanted cotton is then entered into the acetic acid solution of the Phthalogen complex. Exhaustion of the cold dyebath is fairly rapid, but in this acetic acid solution Phthalogen complexes impart only a weak tint to the material.

As practically no levelling takes place during dyeing, the main consideration is to ensure that the Phthalofix FN is taken up evenly by the fibre. The material should be agitated thoroughly after entering the dyebath, so that the dyes are absorbed evenly by the anionic fixing agent. A fixed ratio of Phthalofix FN to dye should also be maintained. After dyeing, the goods are rinsed thoroughly and placed in a fresh bath containing, per litre, about 5 c.c. caustic soda and 2 g. sodium hydrosulphite, at 60–70°C. (140–158°F.). Development of the phthalocyanine is almost immediate. Much of the Phthalofix FN is removed from the material in this reducing bath, and subsequent soaping at b.p. serves the dual purpose of improving the fastness to rubbing and removing any residual Phthalofix FN. An acid treatment, which is best given between the reduction and soap baths, increases the clarity of the colour. This process has so far produced good results on hanks, cheeses and terry fabrics (winch-dyed). Trials aimed at using this process for other piece goods, either on the winch or the jig, are still in progress.

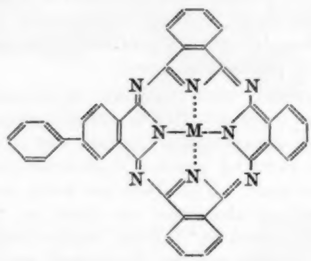
In general, the above method of dyeing gives fastness properties which are equal to those obtained by pad dyeing or printing. The only difference, with both Phthalogen Brilliant Blue IF3GK and Phthalogen Turquoise IFBK dyeings, is that the fastness to light (*B.S.* 1006 : 1955) is about one grade lower, although in pale depths it reaches 6–7 and is as high as 7 in one-third standard depth. The dyes have very good fastness to washing, soda boiling and peroxide bleaching. The fastness to chlorine is only moderate, whilst the fastness to rubbing is dependent on the duration of the soaping treatment, as well as on the type and cleanliness of the material. Nevertheless, it is quite possible to obtain satisfactory fastness to dry and wet rubbing. The method can also be used for dyeings of equally good fastness on viscose rayon.

Application to Silk— With silk, no preliminary treatment with Phthalofix FN is necessary, but thorough degumming, and removal of degumming residues by careful rinsing, is essential for obtaining uniform results. Development of the phthalocyanine is carried out in a formic acid bath containing Decrolin Sol. Conc. (C.I. Reducing Agent 6). This is followed by souring and thorough soaping. Very bright blues and turquoise blues are obtained with both dyes, which are notable for their good fastness to light, washing, boiling-off and peroxide bleaching.

Time Factor and Stability— The critical stage of this process is the preparation of the dyebath. The stock solution must not be allowed to stand for much longer than the 20 min. needed to make it ready for use. The stability limit is about 2 hr., so there is sufficient latitude for cases in which it is better to add the stock solution to the dyebath in portions. As soon as the diluted dyebath has been prepared, however, hydrolysis begins, so it is imperative, in order to obtain consistent results, to work to a time-table which enables the Phthalofix-prepared material to be entered into the dyebath immediately it has been prepared for use.

Phthalocyanine-related Tetra-azaporphin Derivatives

The example of mixture dyeings with Phthalogen Brilliant Blue IF3G and Phthalogen Brilliant Green IFFB[5] has shown that the monomeric diiminoisoindolines are capable of condensing with each other to give phthalocyanine molecules in which substituted and unsubstituted 1,3-isoindoline and 1,3-pseudoisoindole radicals are linked together—



There has been no lack of effort to obtain compounds related to the diiminoisoindolines in order to achieve variations of the phthalocyanine molecule possessing different hues. Numerous interesting new dyes have been discovered during laboratory work based on this principle. In theory there are many possibilities of introducing substituents into the benzene ring of the isoindolines, and of substituting heterocyclic rings for the benzene rings. However, there are very considerable difficulties in a synthesis of this kind on the technical scale.

PHTHALOGEN BRILLIANT BLUES IFGM AND IRM; NAVY BLUE IRRM; AND BLUE-BLACK IVM

The development of the parent compound of these new Phthalogen brands was a considerable technical achievement. These dyes are comparable in structure and composition to the monomeric isoindolines, Phthalogen Brilliant Blue IF3GM

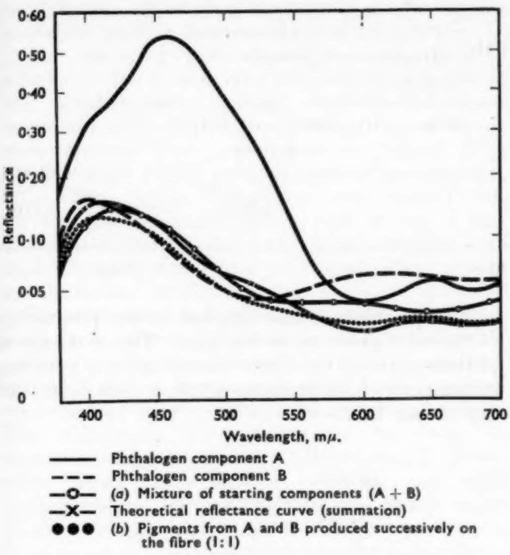
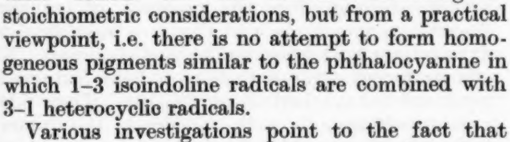


Fig. 6

and Phthalogen Turquoise IFBM. However, they do not consist of an individual diiminoisoindoline and a metal complex (Phthalogen K or NI), but are mixtures of diiminoisoindoline and a similar monomeric primary product, together with different amounts of the above metal complexes.

The compound forming the basis of these dyes has not been marketed as an individual product. It is a monomeric compound, similar in structure to the diiminoisoindoline, but with an extra heterocyclic ring. On condensation to a polymeric tetra-azaporphin, with copper as a central atom, it gives dull violet colours, and with nickel as the central atom a violet–black. Overall fastness is surprisingly high. Phthalogen Navy Blue IRRM, which contains a copper complex (Phthalogen K), and Phthalogen Blue Black IVM, which contains a nickel complex (Phthalogen NI), are the most important commercial products. The ratios in these brands are not selected according to stoichiometric considerations, but from a practical viewpoint, i.e. there is no attempt to form homogeneous pigments similar to the phthalocyanine in which 1–3 isoindoline radicals are combined with 3–1 heterocyclic radicals.

Various investigations point to the fact that mixtures of pigments result from the above Phthalogen primary products during condensation to the dyes on the fibre. These mixtures contain homogeneous products, i.e. dyes built up and combined in each case from only one kind of monomer, or, alternatively, built up from both types of monomers. The following formulae illustrate the various possibilities—

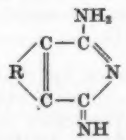


Pure phthalocyanine | 3 : 1 | 1 : 1 | 1 : 3 | Pure heterocyclic

Reflectance curves support the assumption that these ring systems are formed during condensation. Comparison of reflectance curves for (*a*) a dyeing produced from a mixture of both monomers, and (*b*) a dyeing obtained by producing the homogeneous pigments in sequence, i.e. in two separate operations in which the same ratio of the components is maintained, indicates a characteristic deviation of the curve of (*a*) compared with that of (*b*). Curve (*b*) in Fig. 6 has a shape which agrees well with the curve obtained by combining the reflectance curves of the individual dyes.

APPLICATION OF PHTHALOGEN M DYES

The chemical principle forming the basis for the application of the new Phthalogen M brands is the same as that for the monomeric diiminoisoindolines. Accordingly, the behaviour of the new brands is very similar to that of Phthalogen Brilliant Blue IF3GM. The new component contained in the mixtures is a monomeric aminoiminopyrrolenine—



(R = part of a heterocyclic ring) and shows the same chemical behaviour as 1-amino-3-iminopseudoisoindole. The main reaction, polycondensation, which proceeds by elimination of ammonia and reduction to the pigment, requires the application of heat in a solvent medium of poor volatility (Levasol P, PO or F). Phthalogen Blue Black IVM requires only Levasol F (formamide) for condensation, although good yields can also be obtained by adding Levasol P or PO. For reasons of economy the proportion of the cheaper formamide is kept as high as possible. Thus with a 5% print of Phthalogen Navy Blue IRRM, 95 parts of Levasol F, together with only 5 parts of Levasol PO, can be used. These ratios apply to direct printing and to polycondensation in steam. Conditions are slightly different when padding is followed by polycondensation in a curing range. However, work in this connection has not yet been completed. It is possible to obtain piece dyeings by padding with solutions having a similar composition to the printing pastes, development to the pigment taking place either in steam or in a curing range (5–8 min. at 266–284°F.).

The aminoiminopyrrolenine in the mixtures, like 1-amino-3-iminopseudoisoindole, hydrolyses in aqueous liquors and in printing pastes, so its stability is limited. Cool storage in the dark helps to retard decomposition.

Since the heterocyclic compound reacts with amines, it can be resisted, but practical recipes for resist styles have not yet been successfully developed for all the mixtures.

MULTI-COLOUR PRINTING ALONGSIDE DYES OF OTHER CLASSES

As with Phthalogen Brilliant Blues IF3G and IF3GM, the new products are affected by volatile compounds from Aniline Black prints, blue prints

turning green. They are also susceptible to vapours resulting from the steaming of vat prints applied by the potash–sulphoxylate formaldehyde method, unless polycondensation has reached an advanced stage before steaming, as the result of high-temperature cylinder drying. Printing in conjunction with vat dyes by the potash–sulphoxylate formaldehyde method is also restricted by the fact that the dyes have a detrimental effect upon each other. Fall-on prints are not possible, and even in fitted patterns some effect on the colours is noticeable. The products can be applied alongside vat dyes by the two-phase (Colloresin) process if the Phthalogen M dyes are developed in dry heat or steam before passing through the reducing bath.

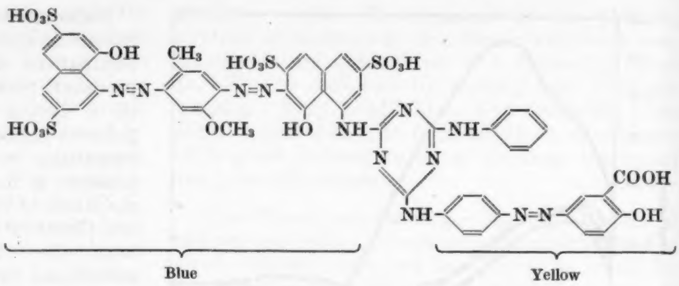
The new products can be printed on a naphtholated ground in the same way as Phthalogen Brilliant Blue IF3G.

The leuco esters of vat dyes, Rapidogens and pigments provide complementary colours in multi-colour printing. Particular attention is drawn to Phthalogen Blue Black IVM as an outline black. It can be printed first, as it is very little affected by "crushing". Alongside Rapidogens it possesses the advantage of not affecting the coupling of these dyes when overprinted or overlapped. It does not soil white grounds during rinsing, and it is especially suitable as an outline black in Phthalogen Brilliant Blue IF3G resist prints.

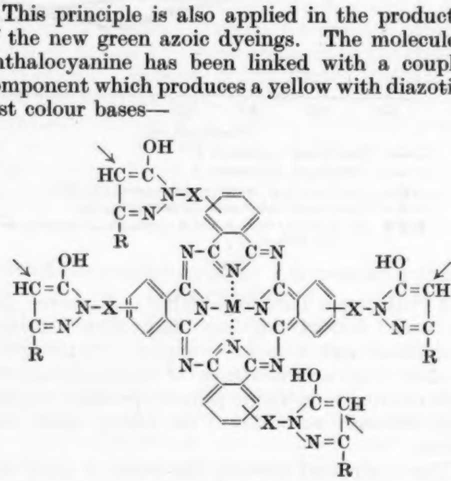
Naphthol AS-FGGR

This new product, from the point of view of application technique, belongs to the azoic class of dyes, but its outstanding properties, viz. clarity of colour and high fastness to light, can be attributed to the phthalocyanine ring from which it is derived. For the first time the range of azoic coupling components includes a member which provides clear yellowish greens possessing good overall fastness properties. The production of this coupling component on a technical scale in the degree of purity indispensable for obtaining high fastness properties is the outcome of many years of co-operation between chemists and colourists.

Two basic possibilities are available in the synthesis of green dyes. Firstly, blue chromophores can be modified by suitable substitution, or polynuclear condensation, so that there is a bathochromic shift towards green. Typical examples are Caledon Jade Green XBN (dimethoxydibenzanthrone), Phthalogen Brilliant Green IFFB (tetraphenyl-Cu-phthalocyanine) and Naphtol AS–GR→Fast Blue BB (3-hydroxy-2-*o*-anthrotoluidide coupled with 4′-amino-2′,5′-diethoxybenzanilide). The other way of obtaining homogeneous green dyes is by linking a blue component with a yellow component by means of a suitable intermediate, as in Chlorantine Fast Green BLL (C.I. Direct Green 26)—



This principle is also applied in the production of the new green azoic dyeings. The molecule of phthalocyanine has been linked with a coupling component which produces a yellow with diazotised fast colour bases—



This combination of a blue dye and a yellow dye in the same molecule gives pure greens of remarkable tinctorial strength.

Another effect of combining blue and yellow chromophores within a molecule is the resultant fastness to light. Fortunately, the yellow part of the Naphthol AS–FGGR molecule is also very fast, so good overall fastness to light is obtained and there is no change of hue to blue on prolonged exposure. The clear greens obtainable with a number of azoic diazo components possess a fastness to light of at least 6. They also withstand very severe washing, even in presence of oxygen-liberating compounds, and they are insensitive to dry and wet heat when ironing and steaming. No change in colour or reduction in light fastness is produced by synthetic-resin finishes. Their fastness to chlorine is only moderate, the colours becoming bluer and weaker.

PROPERTIES OF NAPHTHOL AS–FGGR

Naphthol AS–FGGR is a stable, water-insoluble, greenish-blue powder. With a little caustic soda it can be dissolved readily, in concentrations of up to 100 g./litre, and greenish-blue solutions of extremely good stability are obtained.

The naphtholate has practically no affinity for cellulosic fibres. In exhaustion tests with dry cotton yarn, some increase in concentration is apparent in the residual liquors, hence water, but very little naphtholate, penetrates into the fibre capillaries. Colorimetric determination of the

naphtholate in solution is possible, as Beer's law is obeyed up to a concentration of 0·1 g./litre.

The following tests showed that the lack of affinity is due to the very low rate of diffusion of the naphtholate. Cotton, continuous-filament cuprammonium rayon and viscose rayon staple were treated with a solution containing 20 g. Naphthol AS–FGGR per litre, at room temperature, 50°C. and 95°C. Treatment was carried out (a) for the usual immersion time of ca. 1 sec., (b) for 1 hr., and (c) for 2 hr. The materials were then mangled, dried and developed. The results are illustrated in Fig. 7.

The differences in depth for the various temperatures and immersion times are least noticeable with cotton, but at medium and high temperatures, in particular, a longer immersion time improves the build-up of the naphtholate to some extent. The differences are greater in the case of cuprammonium rayon; dyeings are much deeper after longer immersion at medium and high temperatures. Viscose rayon staple shows much poorer dyeing, but the effect of longer immersion is visible at 50°, and clearly evident at 95°C. These results are in accordance with the familiar fact that viscose rayon fibres offer the greatest resistance to diffusion, owing to their skin.

These tests showed that high temperatures and the longest possible immersion assist the naphtholate to penetrate into the interior of the fibres. Photomicrographs of cross-sections of cuprammonium fibres taken from the dyeings (Fig. 8) confirmed that penetration increases with rise in temperature and duration of treatment.

One special feature of Naphthol AS–FGGR is the relative insensitivity of the naphtholate to hydrolysis and to the carbon dioxide in the air. It is not advisable to use formaldehyde in the impregnating baths, but the impregnated goods should not be exposed to light for any length of time, since this can lead to decomposition.

Owing to its lack of substantivity, Naphthol AS–FGGR is only suitable for padding. Satisfactory dyeings are obtained on cotton cloth, in spite of the low rate of diffusion, but not on viscose rayon. Presumably, the naphtholate diffuses into the cotton fibres during drying, but not into viscose rayon.

Owing to lack of substantivity, the naphtholate tends to migrate during drying. The best type of intermediate drying plant is a hot-flue dryer working at 140–194°F., depending on the running speed. Ventilation by air circulation should be even, and local overheating must be avoided. Modern hot-flue dryers give uniform dyeings which meet most requirements. The migration tendency can be counteracted by adding 30 g. Glauber's salt per litre of impregnating liquor.

DEVELOPMENT OF NAPHTHOL AS–FGGR

The rate of coupling of Naphthol AS–FGGR is so high that no special measures are needed for accelerating coupling. It is sufficient to give the usual air passage after the cloth has left the developing pad. An increase in the concentration of acetic acid in the developing baths has no detrimental effect on yield. The usual azoic diazo components yield colours ranging from brilliant green to black–brown, *via* a yellowish olive-green and a moss green. Of chief importance are the clear greens of high fastness to light which are obtained with azoic diazo components containing the trifluoromethyl group (Fast Orange Bases GGD and RD), and with chloroanilines, chlorotoluidines and chloroanisidines (Fast Yellow Base GC, Fast Red Bases KB and TR, Fast Scarlet Base TR, and Fast Red Base RC). In order to obtain pure colours and the best possible fastness to washing and rubbing, careful aftertreatment in the usual hot soap and soda ash bath is necessary. The clear green is just as bright in artificial light as in daylight, but it is slightly bluer.

APPLICATION IN TEXTILE PRINTING

The printing of Fast Bases on Naphthol AS–FGGR grounds is of little interest as, apart from green, only a few dark browns can be obtained, and the fastness of these is slightly inferior. In addition, the naphtholate is too difficult to remove by the usual alkaline treatment.

DISCHARGE PRINTING

It is possible to discharge the clear greens obtained with Naphthol AS–FGGR, but special recipes are necessary. The residues arising from discharge printing are pale grey and, in the case of white discharges, must be rendered water-soluble by adding Leucotrope W. Depending on the depth of the ground shade, 50–100 g. Leucotrope W are required per kg. of discharge paste, which should also contain anthraquinone. Coloured discharges can be obtained by using selected vat dyes. Thus, fairly bright reds are obtainable with Indanthren Brilliant Scarlet E3G, 10–20 g. anthraquinone (30%) per kg. of paste being added to increase the discharge effect. Since Leucotrope W has an adverse effect on coloured discharges, complete removal of the light grey reduction products is impossible, so yellow prints have a slightly dull appearance. In general, it is advisable to treat the discharge grounds with Ludigol, in order to prevent scumming and doctor streaks. After steaming, the coloured discharges are developed in the usual manner by oxidising, rinsing and soaping thoroughly.

Rapidogen Printing

The most important field of application is probably direct printing by the Rapidogen method. Using the water-soluble diazoamino compounds of some Fast Bases, it is possible to obtain Rapidogens with Naphthol AS–FGGR. At present there are three brands on the market, viz. Rapidogen Brilliant Greens I5G, I6G and N–I6G, of which the first two are developed in acid steam and the third in neutral steam. These Rapidogen brands give greens which are as bright and as fast as the dyeings obtained with Naphthol AS–FGGR.

Printing pastes are prepared by the method generally used with Rapidogen dyes. A good solvent, as far as yield is concerned, is Glyecin A (thiodiglycol), but industrial alcohol or

Cellosolve can be used without impairing tinctorial strength to any extent. With Rapidogen Brilliant Greens I5G and N–I6G it is advisable to add urea. It has also proved advantageous with the latter dye to add potassium sulphite and neutral chromate in order to maintain clarity of colour; these chemicals show good compatibility in an alkaline medium. Printing pastes containing Rapidogen Brilliant Greens I5G and I6G are stable for at least 30 days, but pastes containing the N–I6G brand are stable for only 5–8 days, depending on temperature.

These dyes can be printed alongside other dyes in the same way as familiar Rapidogen brands, e.g. alongside Aniline Black, vat dye leuco esters, Phthalogen dyes and (preferably using the N–I6G brand) reactive dyes. They are also suitable for resists under Aniline Black, using zinc oxide (or zinc oxide and potassium sulphite) as the resisting agent.

Naphtholate Printing

Naphthol AS–FGGR may well give new life to the naphtholate printing technique, which is scarcely used nowadays. By this method it is now possible to develop the yellow, red, brown, black and green naphthols with a Fast Red Base to give a range of colours including yellow, golden yellow, orange, scarlet, red–bordeaux, brown, green and black. There is no blue in this range, but it is possible to apply Phthalogen Brilliant Blue IF3GK and Phthalogen Turquoise IFBK with bisulphite by the wet developing method.

The Naphthols and Phthalogen dyes are printed on the cloth, which is then dried, padded with the Fast Red Base, given a short air passage, treated in one or two baths of boiling bisulphite solution, rinsed thoroughly and soaped at b.p. Yellow and green Naphthols can be mixed to obtain yellowish green and lime shades.

CONCLUSIONS

Although Naphthol AS–FGGR is a welcome addition for piece dyeing, and for direct and discharge printing, there are still gaps to be filled in connection with the dyeing and printing of viscose rayon. The substantivity needed for dyeing yarns in a long liquor has not yet been achieved, and there is need for greater fastness to chlorine.

* * *

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FARBENFABRIKEN BAYER AG.
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GERMANY

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PUBLICATIONS SPONSORED BY THE SOCIETY'S FASTNESS TESTS CO-ORDINATING COMMITTEE—XXIX

The Determination of Colour Fastness to Dry-heat Pleating and Setting

HEAT TREATMENTS SUBCOMMITTEE

The possibility of using existing tests for the measurement of colour fastness to dry-heat setting, or pleating, is discussed. A new test for measuring colour fastness to dry-heat setting and pleating is described, and factors influencing the results obtained with the new test have been investigated. The new test has been compared with other proposed tests for measuring colour fastness to dry-heat setting and pleating and good agreement has been found.

The introduction of hydrophobic synthetic fibres and new resin finishes for cellulosic fibres has resulted in a demand for dyed materials possessing high colour fastness to pleating and setting processes. The Pleating Fastness Subcommittee, now known as the Heat Treatments Subcommittee, has already published a report dealing with steam pleating processes[1], and the method of testing proposed has been accepted as a test "Under Discussion" by the International Organisation for Standardisation (I.S.O.). The present report deals with work leading to a proposed test for colour fastness to dry-heat pleating and setting processes, and details of a proposed test are given. It must be emphasised that this proposed test has not yet been discussed by I.S.O. and, as other organisations have also formulated provisional tests, it would be premature to assume that the ultimate I.S.O. test will follow the lines suggested. Nevertheless, the Subcommittee considers that the test proposed is attractive because of its simplicity, and the Society of Dyers and Colourists will recommend its adoption by I.S.O.

1. Preliminary Considerations

The Society and the AATCC have already published tests for the assessment of colour fastness to dry heat. The S.D.C. test[2], *Colour Fastness to Pressing: Hot Pressing: Dry Pressing* (which is ISO Recommendation R105, Part 17) involves pressing the material for 15 sec. with a flat-iron to give a pressure of 30 g./sq.cm. (0·43 lb./sq.in.) at one of three selected temperatures. The temperatures were selected for (*a*) cotton and linen, (*b*) wool, silk and viscose rayon, and (*c*) acetate rayon and polyamide fibres. Assessment is made

of change of shade immediately after treatment and after conditioning for 4 hr., as well as of staining of adjacent cotton cloth. The AATCC test [3], *Colour Fastness to Dry Heat*, is very similar except that two sets of conditions only are specified, viz. 5 sec. at 218°C. (424°F.) to assess the colour change of the test pattern, and 10 sec. at 177°C. (351°F.) to assess staining of adjacent press-cloth.

It would obviously be desirable if one of these tests could be adopted to assess the colour fastness to setting and pleating processes. Both tests were considered by the Subcommittee and experimental work was carried out to provide information. As a result of this work both tests were rejected as a basis for a suitable test for assessing the colour fastness to setting and pleating processes, for the following reasons—

(1) Flat-irons gave non-reproducible results, even when the surface temperature was controlled with a pyrometer. Moreover, the surface temperature of an electric iron showed large variations at different positions on the surface. It was therefore difficult to define an accurate temperature for the test. In addition, some difficulty was experienced in using normal "contact-type" laboratory thermocouple pyrometers for obtaining a reliable measurement of temperature. Non-reproducibility was found mainly in staining of adjacent fibres.

(2) Cotton was found to be unsuitable as an adjacent white material in many cases, as it frequently failed to stain, even though dye sublimed off the test material during the test.

(3) The specification of temperatures for different materials was not considered completely satisfactory, as blends of fibres are now very common. In addition, the range of fibres specified does not now cover the range of fibres available and, indeed, in this respect it would be difficult to keep pace with the introduction of new fibres.

(4) The specification of different times and temperatures for assessing the effect of the test on the coloured textile and the staining of adjacent material, as in the AATCC test, was considered undesirable.

(5) It was held that a colour fastness test for assessing fastness to setting and pleating processes was not concerned with "ageing" and, therefore, assessment should take place at least 4 hr. after the test, and not immediately and 4 hr. after the test as in the I.S.O. test.

Another standard test which could, perhaps, be extended to determine the colour fastness to setting and pleating processes is the ISO Draft Proposal *Colour Fastness to Sublimation in Storage* [2]. This test is valuable for assessing the resistance of a coloured textile material to dry heat under mild conditions for a long period (5 hr. at 120°C. (248°F.)). Dry-heat setting and pleating processes are, however, essentially very rapid treatments under severe conditions. It is by no means certain that a good correlation exists, on all fibres likely to be subjected to the short-period severe treatment, between short times at high temperatures and long periods at low temperatures. Indeed, evidence has been obtained [4] which shows that the outward diffusion and sublimation of dye from a fibre is related to the mobility of the fibre molecules. The state of internal mobility of the fibre is not necessarily related in a linear manner with temperature, and may also vary from fibre to fibre. For this reason exposure for longer periods and lower temperatures than those normally used in practice is a questionable procedure, and the Subcommittee considered that a test was desirable which gave a direct measure of the fastness of the coloured textile under the conditions of pleating or heat setting without the need to make important assumptions. For these reasons the sublimation test was rejected as a means for determining the fastness to pleating or heat setting.

2. Preliminary Alternative Tests

The Subcommittee agreed that any tests selected should cover the following requirements—

(1) They should be reproducible. It was thought that accurate control of temperature was probably the main requirement, but other factors which may be important are evenness of contact between the test pattern and the adjacent white material, and pressure of contact

(2) They should be simple and, if possible, avoid the use of special or expensive apparatus

(3) The results should be capable of quantitative assessment using the ISO Grey Scales

(4) The tests should be suitable for all types of textile materials.

It was considered that, in order to satisfy requirement (2), the apparatus should, if possible, avoid the use of thermocouple pyrometers. The experience of members of the Subcommittee in the use of instruments of this type for measuring the temperatures of metal surfaces had shown that, unless these instruments were adequately maintained and unless there were facilities for frequent checking of accuracy, their use could lead to inaccurate results. Whilst the larger organisations would not find difficulty in checking these instruments, smaller firms would probably not be in a position to provide the necessary servicing. Consequently, the Subcommittee considered that, if at all possible, temperature measurements should be made with mercury-in-glass thermometers.

In one attempt to use a mercury thermometer for temperature measurement, a stainless steel beaker, approximately 12 cm. in diameter, was filled with a low melting-point metal alloy. The material to be tested was sandwiched between adjacent white fabrics, and the beaker containing the molten metal, at an agreed temperature, was placed on the sandwich for an agreed time. In effect the beaker was used in the same way as a

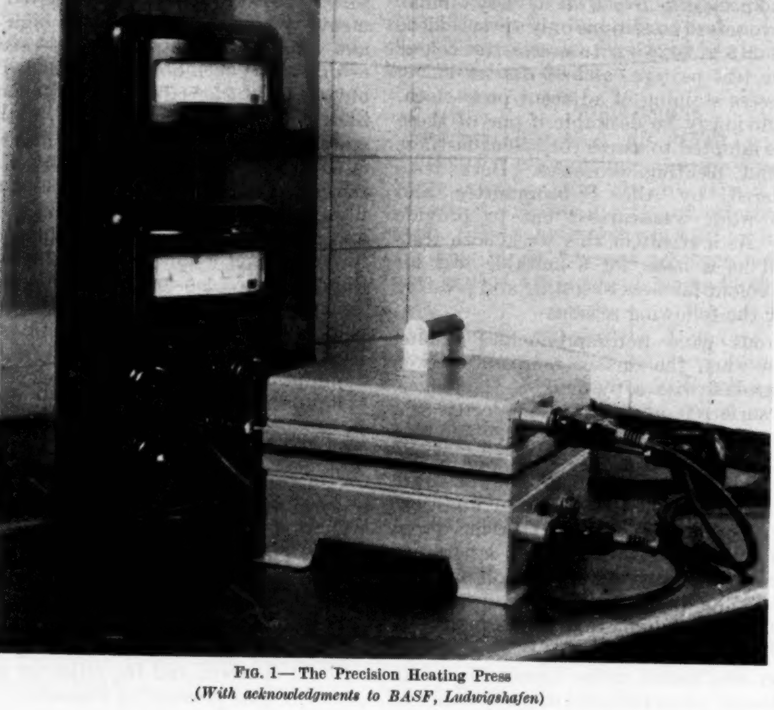

FIG. 1—The Precision Heating Press
(With acknowledgments to BASF, Ludwigshafen)

FIG. 2—The Thermotest Rhodiaceta
(With acknowledgments to Etab. D.A.M., Lyons)

flat-iron, except that the temperature of the molten metal could readily be measured with a mercury thermometer. This method was rejected as the results obtained were not reliable. The method suffered from some of the defects found when using a flat-iron; there was uncertainty about the heated surface, probably caused by poor conduction and the cooling effect of the unheated stand on which the patterns were placed. In another attempt—which failed for similar reasons—a heated metal block was used, a narrow hole being drilled into the centre of the block to take a mercury thermometer immersed in a conducting liquid.

At this stage, although realising the drawbacks, the Subcommittee again considered the use of electrically heated plates with the temperature being measured by thermocouples. The essential requirements were that both the top and the bottom plate should be heated and the temperature should be measured, and that the plates should be large enough to allow side-by-side tests to be carried out. In addition, the temperature of the plates should be controllable. Before an instrument was constructed, the Subcommittee received information about an instrument designed by the Deutsche Echtheitskommission. This instrument, which is illustrated in Fig. 1, is described as a *Precision Heating Press*; as it incorporates most of the features thought to be desirable, it was regarded with favour by the Subcommittee, since acceptance of this design might assist in reaching rapid agreement at I.S.O. Another apparatus, the *Thermotest Rhodiaceta*, is supported by the Institut Textile de France; it has been fully described [5] and is illustrated in Fig. 2. In this instrument there are 13 small, electrically heated plates which rest on unheated plates. The temperature of the two end upper-plates is measured by means of a thermometer, and the temperature of the intermediate plates is calculated from a knowledge of the electrical system. Although it was agreed that this instrument was much more satisfactory than an electric iron, it was not favoured by the Subcommittee, for the following reasons—

(1) The uncertainty regarding the temperature of the intermediate plates

(2) The fact that there is direct heating of the upper plate only

(3) The high cost of the apparatus

(4) The difficulty of carrying out side-by-side tests

(5) The danger of excessive data making interpretation difficult—one test could give 12 figures for effect on shade and staining of two adjacent white fabrics

(6) The length of time required for the instrument to warm up before use (4 hr. approx.)

At this stage, a meeting of the Colour Fastness Subcommittee ISO/TC 38/SC 1 took place in Lucerne. No firm proposals for a colour fastness test for dry pleating or heat setting were made at this meeting, but it was agreed that the German Precision Heating Press and the French Thermotest should be examined fully, testing temperatures of 150°C. (302°F.), 180°C. (356°F.) and 210°C. (410°F.) being accepted. Later the Heat Treatments Subcommittee and the Institut Textile de France agreed that the preferred time of heating should be 30 sec. It was also agreed to investigate the effect of pressure of contact on the degree of staining of adjacent undyed fabrics.

3. Proposed S.D.C. Testing Method

3.1 About this time Mr. S. N. Bradshaw, a member of the Heat Treatments Subcommittee, suggested that reproducible tests could be obtained by immersion of the test material, sandwiched between adjacent white fabrics and held in a suitable holder, in molten metal at the agreed temperature. This method of test, if proved suitable, would possess many advantages. It was therefore decided to determine whether a suitable test could be devised on the basis of immersion in molten metal.

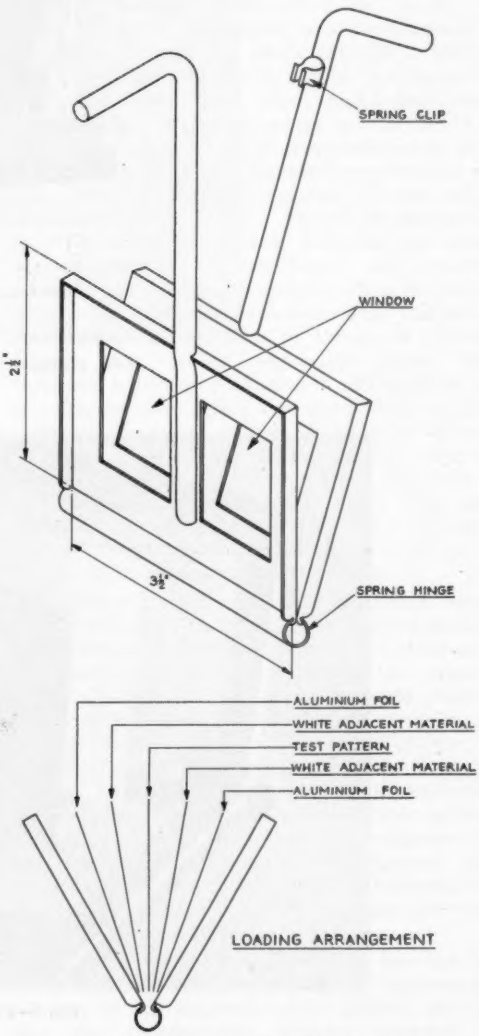

FIG. 3—Construction and Loading of Holder

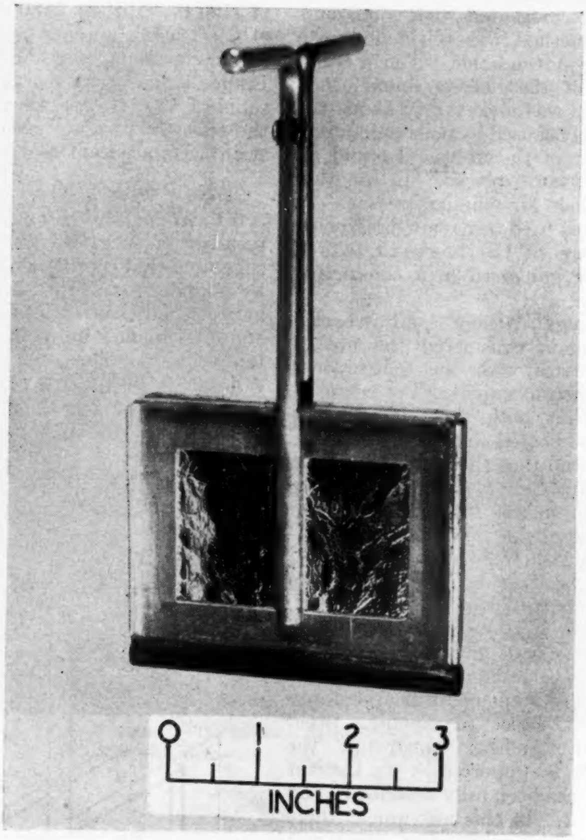

FIG. 4— Holder containing Fabric Sandwich

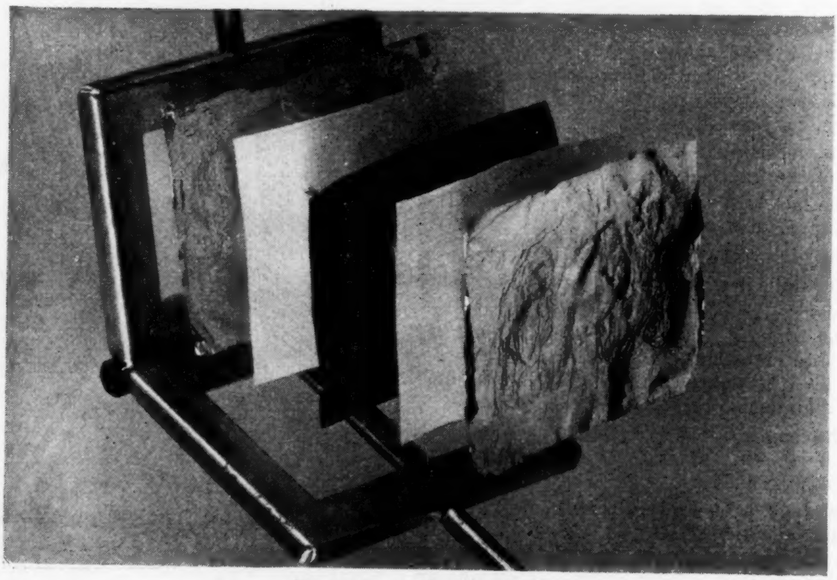

FIG. 5— Use of Aluminium Foil

3.2. CONSTRUCTION OF APPARATUS

A holder was constructed in which the "fabric sandwich" was held between two aluminium plates. The plates were hinged at one end and, after insertion of the fabric sandwich, were held together at the other end by means of a spring clip. Both aluminium plates had "windows" cut in them in order to allow contact of the fabric sandwich with the molten metal. The size of the holder is not important, whilst the number of windows in the aluminium plate can be increased if desired, depending upon the number of tests required at any one time. The construction of the apparatus is illustrated in Fig. 3 and 4.

The alloy used contained 10% Cd, 13·4% Sn, 50% Bi and 26·6% Pb, and melted at 71°C. (140°F.) approx. One difficulty in this test was that the molten metal sometimes stuck to the outside of the fabric sandwich and soiled the adjacent whites. This difficulty can be overcome by placing two sheets of aluminium foil (0·001–0·002 cm. thick and 1·0 cm. approx. larger than the adjacent white fabric) over each side of the sandwich, as illustrated in Fig. 5. The aluminium foil prevents soiling by the molten metal and, as it is very thin, heat is very rapidly conducted through the material. It is advantageous to use fresh foil for each test.

3.3. VARIABLES IN TEST

3.3.1. *Effect of Pressure*

At the I.S.O. meeting in Lucerne there was some discussion on the effect of pressure on the results of the dry-heat test when using either the Thermotest or the Precision Heating Press instruments. A pressure of 30 g./sq.cm. was suggested for initial tests by the French. The effect of pressure was investigated by immersing the test pattern, contained in the holder, at varying depths in the molten metal. On the dyed material used for the test, which showed a stain of 3 (on to adjacent Terylene) at 180°C. (356°F.), pressures between 10 and 80 g./sq.cm. did not cause any change in the degree of staining or in the effect on the dyed pattern. It is thought that the function of pressure is merely to ensure even contact between the test patterns and the adjacent white materials and is not otherwise important. One of the advantages of a fluid metal surface, compared with a heated solid surface, is the uniform pressure obtained on the patterns, which results in very even staining of adjacent materials. Although pressure of contact is clearly not important, a mean depth of immersion corresponding to a pressure between 30 and 80 g./sq.cm. is recommended.

3.3.2. *Effect of Constitution of adjacent White Fabrics*

In a dry-heat test the degree of staining of the adjacent white fabric is clearly important. Using a wide range of disperse-dyed fabrics, including nylon, triacetate rayon and Terylene, the staining of adjacent white materials composed of nylon, Terylene, triacetate rayon and viscose rayon was investigated. In every case where staining took place, the heaviest staining was observed on the Terylene. It is therefore suggested that one of the adjacent white fabrics should always be of Terylene, and the other should be of the same material as that under test. It is important to specify the nature of both adjacent white materials. During the heating, certain white textile materials change shade slightly, e.g. a severe heat treatment will result in a slight yellowing of nylon. When assessing the results for staining of adjacent white materials, it is important to assess the staining against white fabric which has been similarly heated in the absence of coloured fibre, so as to eliminate the effect of fabric discoloration.

3.3.3. *Effect of the Physical Properties of the Fabric*

In the proposed method of measuring the colour fastness to dry-heat treatments, the heat is conducted through the adjacent white fabrics to the test pattern. As the proposed time of heating is only 30 sec., it might be expected that the thickness of the adjacent white materials, by affecting the heat transfer, would affect the result. The effect of fabric thickness was investigated by carrying out tests for 30 sec. at 150°C. (302°F.), 180°C. (316°F.) and 210°C. (410°F.) on samples of triacetate fabric dyed blue, violet and orange respectively. Adjacent white nylon (0·014 cm. thick) and adjacent white triacetate rayon (0·028 cm. thick) were used. Tests were carried out with one, two and three thicknesses of each of the adjacent white materials. The results showed that only the surface in contact with the test pattern was stained and that, surprisingly, there was only a very slight decrease in staining when the number of adjacent fabrics on each side of the test pattern was increased from one to three. It therefore follows that, within reasonable limits, fabric thickness is not very important, although (to take an extreme case) if felt were used as the adjacent material the result would probably be seriously affected. It was therefore suggested that the adjacent material should be not less than 0·01 cm. and not more than 0·06 cm. thick. The lower limit is suggested as one which gives a reasonably opaque fabric: the higher limit is based on the results of the experiments described.

The fibre diameter and the delustrant content can affect the optical properties of dyed material. An increase in fibre diameter and a decrease in delustrant content both increase the apparent depth of a dyed material, so both should affect the degree of staining of adjacent white materials, but tests have shown that the degree of staining, as measured on the ISO Staining Scale, is not greatly affected by a wide variation in delustrant content or fibre diameter. Nevertheless, in order to avoid the use of extreme conditions, it is suggested that the denier of the fibres in the adjacent white fabrics for a standard test should be between 1 and 10, and the fibre should not contain more than 2·0% titanium dioxide.

The effect of fabric construction has not been studied, as it was not considered important in relation to the adjacent white fabrics, provided that the requirements already discussed are satisfied. If the test pattern consists of yarn or

Table I

Molten Metal Test

Test Pattern	Effect on Shade: Average Assessment	Effect on Shade: Standard Deviation	Staining of Adjacent Fibre I*: Average Assessment	Staining of Adjacent Fibre I*: Standard Deviation	Staining of Adjacent Fibre II*: Average Assessment	Staining of Adjacent Fibre II*: Standard Deviation
Test— 30 Sec. at 150°c.						
Blue knitted nylon	4	0·3	3–4 n	0·2	—	—
Greenish blue knitted nylon	4–5	0·2	5 n	0	—	—
Violet knitted Terylene	3–4	0·5	4 n	0·1	4 Ter	0
Blue woven staple Terylene	4	0·4	4 n	0·1	4 Ter	0
Green woven triacetate rayon	5	0	5 n	0	5 Tr	0
Red woven triacetate rayon	5	0·2	5 n	0	5 Tr	0
Test— 30 Sec. at 180°c.						
Blue knitted nylon	4	0·3	2–3 n	0·4	—	—
Greenish blue knitted nylon	4–5	0·3	4 n	0·2	—	—
Violet knitted Terylene	3	0·3	3 n	0·2	2–3 Ter	0·4
Blue woven staple Terylene	3–4	0·5	3 n	0·3	3 Ter	0·2
Green woven triacetate rayon	4–5	0·5	4 n	0·2	4 Tr	0·3
Red woven triacetate rayon	4	0·6	5 n	0·2	5 Tr	0·2
Test— 30 Sec. at 210°c.						
Blue knitted nylon	3	0·2	1–2 n	0·2	—	—
Greenish blue knitted nylon	4	0·3	2–3 n	0·2	—	—
Violet knitted Terylene	2–3	0·2	2–3 n	0·3	2 Ter	0
Blue woven staple Terylene	3–4	0·5	2–3 n	0	2 Ter	0·3
Green woven triacetate rayon	3–4	0·4	2–3 n	0·3	3 Tr	0·2
Red woven triacetate rayon	3–4	0·4	4–5 n	0·3	4 Tr	0·2

* Tr = triacetate rayon, Ter = Terylene, n = nylon

Table II

Test— 30 sec. at 150°C.

A Comparison with other Testing Methods and with Bulk Pleating Processes

Test Pattern	Conditions of Test	Effect on Pattern	Staining of Nylon I	Staining of Nylon II*	Staining of Other Fibre I†	Staining of Other Fibre II*†
Blue knitted nylon	S.D.C. (molten metal)	4	3–4	—	—	—
	Thermotest	4	3–4	4	—	—
	Precision Press	4–5	3–4	—	—	—
	Bulk Test I	4–5	4	—	—	—
	Bulk Test II	—	—	—	—	—
Greenish blue knitted nylon	S.D.C. (molten metal)	4–5	5	—	—	—
	Thermotest	5	5	—	—	—
	Precision Press	4–5	5	—	—	—
	Bulk Test I	4–5	5	—	—	—
	Bulk Test II	4	5	—	—	—
Violet knitted Terylene	S.D.C. (molten metal)	3–4	4	—	4	—
	Thermotest	4–5	4	4–5	4	4
	Precision Press	4	4–5	—	4–5	—
	Bulk Test I	4	4–5	—	4	—
	Bulk Test II	4	—	—	4	—
Blue woven Terylene	S.D.C. (molten metal)	4	4	—	4	—
	Thermotest	3–4	3–4	4	3–4	4
	Precision Press	3–4	4–5	—	4–5	—
	Bulk Test I	3–4	4	—	4	—
	Bulk Test II	4	—	—	4	—
Green woven triacetate rayon	S.D.C. (molten metal)	5	5	—	5	—
	Thermotest	5	5	5	5	5
	Precision Press	5	5	—	5	—
	Bulk Test I	5	5	—	5	—
	Bulk Test II	5	5	—	5	—
Red woven triacetate rayon	S.D.C. (molten metal)	5	5	—	5	—
	Thermotest	5	5	5	5	5
	Precision Press	4	5	—	5	—
	Bulk Test I	5	5	—	5	—
	Bulk Test II	4–5	5	—	5	—

* In the Thermotest instrument the nylon, or other adjacent undyed fabric, can be either uppermost in the sandwich next to the heated plate or underneath next to the unheated plate. In Test I the nylon (or other fibre) was uppermost; in Test II the nylon (or other fibre) was underneath.

† Triacetate rayon or Terylene as required.

loose fibre, the material is combed out into a smooth pad, as for other fastness tests.

4. Reproducibility of Test

Seven members of the Subcommittee in separate laboratories determined the fastness of 6 dyed materials. The tests were carried out for 30 sec. at 150°C. (302°F.), 180°C. (356°F.), and 210°C. (410°F.), using molten metal according to the proposed specification given in the Appendix, except that nylon was used as the common adjacent white fabric instead of Terylene. After testing, four colourists each assessed all the results so as to eliminate as far as possible errors caused by assessment. The results are given in Table I.

The results obtained are regarded as highly satisfactory. Firstly, it is seen that the standard deviation is small, so that, considering the effect on the pattern, the combined standard deviation is 0·4 and that for staining adjacent undyed fabrics is only 0·2. Thus, for the effect on the pattern, 95% of the results can be expected to be ± 0·8 units from the average result, whilst for staining of the adjacent fabrics, 95% of the results can be expected to be ± 0·4 units from the average result. For colour fastness testing, this degree of reproducibility is high and fully satisfactory for the proposed test.

5. Comparison with Other Testing Methods

In order to assess the molten metal testing procedure and to compare the results with those obtained using methods suggested by other members of Subcommittee ISO/TC 38/SC 1, tests were carried out on the 6 dyed patterns using the Thermotest and Precision Heating Press instruments. The results obtained are given in Tables II, III, and IV. At the same time the 6 test patterns were subjected to a bulk pleating process, and the results of these tests are also recorded. As far as could be arranged, using a Rabo type of dry-heat pleating machine, the times and temperatures of treatment were as specified.

Examination of Tables II, III and IV shows a very high measure of agreement between the three testing procedures, as well as between the laboratory testing techniques and the bulk trials. The results in Tables II, III and IV are summarised in Table V, which shows that, as far as the production of reproducible results is concerned, all

Table III

Test— 30 sec. at 180°C.

A Comparison with other Testing Methods and with Bulk Pleating Processes

Test Pattern	Conditions of Test	Effect on Pattern	Staining of Nylon I	Staining of Nylon II*	Staining of Other Fibre I†	Staining of Other Fibre II*†
Blue knitted nylon	S.D.C. (molten metal)	4	2–3	—	—	—
	Thermotest	2–3	2	2	—	—
	Precision Press	4	2	—	—	—
	Bulk Test I	4	2	—	—	—
	Bulk Test II	—	—	—	—	—
Greenish blue knitted nylon	S.D.C. (molten metal)	4–5	4	—	—	—
	Thermotest	4	3–4	4	—	—
	Precision Press	4	4	—	—	—
	Bulk Test I	4	3–4	—	—	—
	Bulk Test II	4	3–4	—	—	—
Violet knitted Terylene	S.D.C. (molten metal)	3	3	—	2–3	—
	Thermotest	2–3	3–4	3–4	3	3
	Precision Press	3–4	3	—	2–3	—
	Bulk Test I	3–4	3	—	3	—
	Bulk Test II	3–4	—	—	3	—
Blue woven staple Terylene	S.D.C. (molten metal)	3–4	3	—	3	—
	Thermotest	2–3	2–3	3	2–3	2–3
	Precision Press	3	3	—	3	—
	Bulk Test I	3	2–3	—	2	—
	Bulk Test II	3	—	—	3	—
Green woven triacetate rayon	S.D.C. (molten metal)	4–5	4	—	4	—
	Thermotest	4	3–4	4	4	4
	Precision Press	4–5	4	—	4	—
	Bulk Test I	4–5	3–4	—	3	—
	Bulk Test II	4–5	—	—	4–5	—
Red woven triacetate rayon	S.D.C. (molten metal)	4	5	—	5	—
	Thermotest	4–5	4–5	4–5	4	4–5
	Precision Press	4	5	—	4–5	—
	Bulk Test I	4	4–5	—	4–5	—
	Bulk Test II	4–5	—	—	4–5	—

* In the Thermotest instrument the nylon, or other adjacent undyed fabric, can be either uppermost in the sandwich next to the heated plate or underneath next to the unheated plate. In Test I the nylon (or other fibre) was uppermost; in Test II the nylon (or other fibre) was underneath.

† Triacetate rayon or Terylene as required.

TABLE IV

Test— 30 sec. at 210°C.

A Comparison with other Testing Methods and with Bulk Pleating Processes

Test Pattern	Conditions of Test	Effect on Pattern	Staining of Nylon I	Staining of Nylon II*	Staining of Other Fibre I†	Staining of Other Fibre II*†
Blue knitted nylon	S.D.C. (molten metal)	3	1–2	—	—	—
	Thermotest	1–2	1–2	1–2	—	—
	Precision Press	3	1	—	—	—
	Bulk Test I	2	1	—	—	—
	Bulk Test II	—	—	—	—	—
Greenish blue knitted nylon	S.D.C. (molten metal)	4	2–3	—	—	—
	Thermotest	4	2–3	3	—	—
	Precision Press	4	2–3	—	—	—
	Bulk Test I	4	2	—	—	—
	Bulk Test II	4	2–3	—	—	—
Violet knitted Terylene	S.D.C. (molten metal)	2–3	2–3	—	2	—
	Thermotest	1–2	3–4	2–3	3	2–3
	Precision Press	2	2–3	—	2	—
	Bulk Test I	3	2	—	2	—
	Bulk Test II	3	—	—	2–3	—
Blue woven Terylene	S.D.C. (molten metal)	3–4	2–3	—	2	—
	Thermotest	2–3	2	2	1–2	2
	Precision Press	3	2	—	1–2	—
	Bulk Test I	3	1–2	—	1	—
	Bulk Test II	2–3	—	—	2	—
Green woven triacetate rayon	S.D.C. (molten metal)	3–4	2–3	—	3	—
	Thermotest	2–3	2–3	2–3	2–3	2–3
	Precision Press	3–4	2–3	—	2–3	—
	Bulk Test I	3	2	—	2	—
	Bulk Test II	3–4	—	—	3	—
Red woven triacetate rayon	S.D.C. (molten metal)	3–4	4–5	—	4	—
	Thermotest	2–3	3–4	4	3–4	4
	Precision Press	2–3	4	—	4	—
	Bulk Test I	3	3–4	—	2	—
	Bulk Test II	4	—	—	4	—

* In the Thermotest instrument the nylon, or other adjacent undyed fabric, can be either uppermost in the sandwich next to the heated plate or underneath next to the unheated plate. In Test I the nylon (or other fibre) was uppermost; in Test II the nylon (or other fibre) was underneath.

† Triacetate rayon or Terylene as required.

three testing techniques are highly satisfactory. For reasons of cost, simplicity and the absence of a need to check electrical circuits or measuring instruments, the Subcommittee considers that the molten metal test is preferable. Further, the relatively low cost of equipment required should permit its use in laboratories of limited resources where a more elaborate apparatus might be considered unjustifiably expensive. However, where a laboratory has a very large number of tests to carry out, the more convenient, expensive apparatus will offer advantages. The Heat Treatments Subcommittee favours the Precision Heating

TABLE V

Comparison of Testing Methods

(Summary)

Comparison	Average Difference in Result compared with S.D.C. Molten Metal Test: Effect on Pattern	Staining of Nylon	Staining of other Fibre
Thermotest against S.D.C. molten metal test	−0·5	−0·2	−0·2
Precision Press test against S.D.C. molten metal test	−0·2	−0·1	0

Press for this purpose, for reasons already given, and, as is seen in Table V, it gives results closer to those obtained with the molten metal test. If a Precision Heating Press is used, the results obtained should be checked at intervals against those obtained with the proposed molten metal test.

6. A Proposed Test

A proposed test for determining the colour fastness to dry-heat pleating or setting processes has been suggested by the S.D.C. Subcommittee and details are given in the Appendix. It is emphasised that this test has not yet been discussed by I.S.O. and, therefore, no international agreement has been reached.

7. Correlation with Setting Processes

The Subcommittee considers that the proposed test is suitable for assessing the fastness of coloured textile materials to dry-heat setting as well as dry-heat pleating. It is clearly impossible to correlate a treatment for 30 sec. in the molten metal test with all known methods of heat setting. The correlation will prove different for a hot-roll setting machine than for a pin-stenter hot-air

setting frame; indeed, the correlation can be expected to differ where two different hot-air setting frames are compared, owing to differences in machine design. Nevertheless, the Deutsche Echtheitskommission has suggested that the following times and temperatures are comparable—

Test on Precision Heating Press	Stenter Passage
20 sec. at 180°c.	30 sec. at 185°c.
20 sec. at 190°c.	30 sec. at 200°c.

It is hoped that, ultimately, stenter manufacturers may be expected to provide correlation data against agreed I.S.O. conditions for the machine they construct, although such a correlation will only be approximate, as it is likely to vary with the cloth construction.

References

[1] J.S.D.C., **75**, 31 (1959).
[2] *Standard Methods for the Determination of the Colour Fastness of Textiles* (Bradford: Society of Dyers and Colourists, 2nd edition, 1960).
[3] AATCC, *Technical Manual and Year Book*, **34**, 92 (1958).
[4] Bradshaw, S. N., and Ginns, P., Unpublished.
[5] *Teintex*, **22**, 343 (1957).
[6] Document from the Deutsche Echtheitskommission ISO/TC 38/SC 1 (Germany 18), p. 173.

Appendix

Colour Fastness to Pleating: Dry-heat Pleating and Setting

(NEW TEST PROPOSED BY THE SOCIETY OF DYERS AND COLOURISTS)

1. Purpose and Scope

1.1 This method is intended for assessing the resistance of the colour of textiles of all kinds and in all forms to the action of dry-heat pleating and setting processes.

1.2 Three tests differing in severity are provided: one or more of them may be used, depending on the requirements.

2. Principle

2.1 A specimen of the textile in contact with specified undyed cloths is heated in a bath of molten metal. The change in colour of the specimen and the staining of the undyed cloths are assessed with Standard Grey Scales.

3. Apparatus and Reagents

3.1 Specimen holder (see § 7.1).

3.2 Steel beaker to hold specimen holder.

3.3 Hot-plate or sand bath (see § 7.2).

3.4 Metal alloy of the following composition—

Bismuth	50·0%
Lead	26·6%
Tin	13·4%
Cadmium	10·0%

3.5 Mercury-in-glass thermometer reading between 150° and 220°c. (300° and 430°F.).

3.6 Aluminium foil, thickness 0·001–0·002 cm.

3.7 Two undyed cloths, each 4 cm. × 4 cm. and between 0·01 and 0·06 cm. thick, one piece made of the same fibre as that in the textile to be tested, the second piece made of scoured Terylene.

3.8 Grey Scales for assessing change in colour and staining (see § 7.3).

4. Specimens

4.1 If the textile to be tested is fabric, place a specimen, 4 cm. × 4 cm., between the two pieces of undyed cloth (see § 3.7) and sew along one side to form a composite specimen.

4.2 If the textile to be tested is yarn, knit it into fabric and treat as in § 4.1 or form a layer of parallel lengths between the two pieces of undyed cloth (see § 3.7), the amount of yarn taken weighing approximately one-half the combined weights of the undyed cloths. Sew along two opposite sides to form a composite specimen.

4.3 If the textile to be tested is loose fibre, comb and compress an amount weighing approximately one-half the combined weight of the undyed cloths (see § 3.7) into a sheet, 4 cm. × 4 cm. Place the sheet between the two undyed cloths and sew along two opposite sides to form a composite specimen.

5. Procedure

5.1 Condition the composite specimen at 20 ± 2°C. (68 ± 4°F.) and 65 ± 2% relative humidity.

5.2 Cover both sides of the composite specimen with aluminium foil and mount in the holder (see § 7.1).

5.3 Heat the molten metal in the beaker on the hot-plate or sand bath to a temperature such that, when the holder is immersed in it, the temperature falls to the required value (see § 7.2). Three test conditions are specified, viz.—

Mild	**150°C. (302°F.)**
Intermediate	**180°C. (356°F.)**
Severe	**210°C. (410°F.)**

5.4 Immerse the holder containing the composite specimen in the molten metal so that the top of the composite specimen is at least 1 cm. below the surface; leave for 30 sec. Remove the frame from the molten metal, allow to cool, remove the composite specimen and leave for 4 hr. in air at 20 ± 2°C. (68 ± 4°F.) and 65 ± 2% relative humidity.

5.5 Assess the change in colour of the specimen and the staining of the undyed cloths against pieces of the undyed cloths similarly treated in the absence of a specimen, with the Grey Scales (see § 7.3).

6. Report

6.1 Report which test has been used and the numerical ratings for the change in colour of the test specimen, and for the staining of each kind of undyed fibre used.

7. Notes

7.1 The pattern holder should be constructed of aluminium sheet, hinged at one end and with a closing spring clip at the other end. One or more windows, depending upon the number of tests to be carried out at a time, are set into the holder opposite the position for the fabric sandwich to allow rapid heating of the specimen. The construction and mounting of the specimen are illustrated in Fig. 3.

7.2 It is convenient to heat the stainless steel container holding the molten metal on an electric hot-plate or sand bath. It is necessary to heat the molten metal to a temperature somewhat higher than that specified for the test being used, in order to compensate for the cooling caused by the introduction of the frame. The amount of the increase must be determined by calibrating the apparatus used for the three test conditions. It is important to ensure that the temperature of the molten metal is constant throughout its volume.

7.3 See the following sections—

(*a*) *Colour Fastness of Textiles: General Principles of Testing*

(*b*) *Colour Fastness: Grey Scale for assessing Change in Colour*

(*c*) *Colour Fastness: Grey Scale for assessing Staining*

7.4 An account of the development of the test is published in the *Journal of the Society of Dyers and Colourists* as "Publication Sponsored by the Society's Fastness Tests Co-ordinating Committee— XXIX" (J.S.D.C., **76**, 158 (1960)).

COMMUNICATIONS

The Permanent Creasing of All-wool Fabrics*

MARIA A. WOLFRAM and J. B. SPEAKMAN

The optimum conditions for obtaining permanent creases in all-wool fabrics by the method which involves pretreatment with a solution of sodium bisulphite, followed by rinsing, drying at a low temperature and pressing, have been defined. Using a wide range of fabrics, the effects of the process have been compared with those of other methods of achieving the same end.

INTRODUCTION

Fabrics made from yarns prepared by blending Terylene staple fibre and wool in roughly equal proportions are remarkable for the ease with which they can be given permanent creases and pleats by a short period of exposure to superheated steam. Unlike those commonly imparted to all-wool fabrics, the pleats and creases withstand both dry cleaning and washing, and it is not surprising, therefore, that trousers and pleated skirts made from the mixture fabric should have met with such remarkable commercial success.

It was this success which first prompted attempts to obtain permanent creases and pleats in all-wool fabrics. There can be no doubt that the production of such desirable effects should not have had to await the development of Terylene–wool fabrics, because it had been shown, some 20 years before, that the setting of strained wool fibres in steam or aqueous media is assisted by alkalis, sulphites and bisulphites [1]. No attempt had, however, been made to determine which of the many possible reagents would be the most suitable for use by either pleater or tailor, nor to determine the conditions under which it should be used to give maximum set with minimum damage to the fabric.

Both problems can be considered in terms of the chemical mechanism of permanent set, viz. disulphide bond breakdown, which permits main-chain rearrangement and dissipation of stress, followed by rebuilding of linkages between the chains to give permanence to the deformed state of the fibres. The reagents which assist setting do so by promoting disulphide bond breakdown; their presence during linkage rebuilding is not essential and may, indeed, be harmful if, as in the case of alkalis, they are capable of breaking the polypeptide chains. A volatile setting agent has, therefore, special advantages: its concentration is greatest when steam is first introduced, and a high rate of disulphide bond breakdown can thus be realised with little risk of damage during the succeeding rebuilding reaction, because the setting agent, being volatile, is removed during further steaming. A final selection, from among the many setting agents available, was made on the assumption that no process would be acceptable unless the reagent could be incorporated in the fabric by the finisher, so that permanent creases and pleats could be obtained with little or no modification of the methods normally used by the tailor and pleater.

It was in the light of these considerations that bisulphites were selected for use in the following experiments. When strained wool fibres are treated with a boiling solution of sodium bisulphite, the resulting set is due to disulphide bond breakdown and rebuilding [2]. The reaction is conveniently summarised by the following equation—

$$R{\cdot}S{\cdot}S{\cdot}R + NaHSO_3 \longleftrightarrow R{\cdot}SH + R{\cdot}S{\cdot}SO_3Na$$

but it must be understood that main-chain rearrangement follows disulphide bond breakdown, so that the linkages are not normally rebuilt in their original positions, nor from their original components.

As regards the purpose of this investigation, it is fortunate that the breakdown and rebuilding stages of the reaction can be separated. If wool fibres are treated with a solution of sodium bisulphite in the cold, some breakdown of disulphide bonds is brought about—

$$R{\cdot}S{\cdot}S{\cdot}R + NaHSO_3 \longrightarrow R{\cdot}SH + R{\cdot}S{\cdot}SO_3Na$$

and there is only partial reversal of the reaction during subsequent washing [3] and drying, provided that drying is not carried out at high temperatures. If fabric is marketed in this state, creases and pleats can be made permanent simply by the application of steam; the disulphide bonds are then re-formed, and the fibres are permanently set in their deformed state. Only a small amount of combined bisulphite is needed to give this result, because the reagent is liberated during the reverse reaction, and its migration, or that of the sulphurous acid derived from it, leads to further disulphide bond breakdown and rebuilding.

These are the principles underlying the first of the methods developed for imparting permanent creases and pleats to all-wool fabrics [4], and the main purpose of the following experiments was to determine the optimum conditions of treatment in finishing and in subsequent tailoring. The merits of the bisulphite and other processes, including the Siroset process [5] developed in Australia, have also been compared.

Experimental

MATERIALS

The main features of the wide range of fabrics examined are given in Table I.

CREASING PROCEDURE

Patterns (5 in. × $2\frac{1}{2}$ in.) of the various fabrics were immersed for 15 min. at 20° or 40°C. in an aqueous solution of sodium bisulphite containing alcohol (10%, vol./vol.) as antioxidant, the liquor : wool ratio being 18 : 1. The patterns were

* This paper includes part of the lectures given to the Huddersfield and Scottish Sections on 19th January and 12th March 1959, respectively.

TABLE I

Composition and Construction of Fabrics

	Fabric No. 1	2	3	4	5	6	7
Composition ...	27% Mohair 73% Wool	All wool	All wool	All wool	All wool	All wool	Wool with mercerised cotton stripes
Type	Worsted	Worsted	Worsted	Worsted	Flannel	Woollen	Scotch Tweed
Ends/in.	52	80	66	120	52	52	42
Picks/in.	52	80	56	94	52	62	42
Warp counts ...	2/40	2/52	2/30	2/44	28 Y.S.	26 Y.S.	2/24 Y.S.
Weft counts ...	1/20	2/52	2/30	2/44	28 Y.S.	28 Y.S.	1/25 Y.S.
Weight/sq.yd. (oz.)	5	7	8·8	9·8	8·6	10·6	10
Weave	Plain	2/2	2/2	Whipcord	3/3	Duvetyn	Complex

then removed, rinsed three times in tap water, squeezed, and allowed to dry in room air. At this stage each pattern was cut into two 5 in. × 1¼ in. strips, which were folded in two and steamed in the Hoffman press for times ranging from 5 to 60 sec. Standard conditions of pressing were used, some strips being wetted out with water before steaming and others treated in the air-dry state. The strips were cooled in the usual way before they were removed from the press, and the permanence of the creases was then tested.

For purposes of comparison, other methods of obtaining permanent creases were also examined. The general procedure was similar to that described above, except that in one case the two 5 in. × 1¼ in. patterns were simply wetted out in a solution of sodium bisulphite, using a liquor : wool ratio of 2 : 1, squeezed to remove excess solution, folded in two, and pressed for 15 sec. in the Hoffman press. In the second case, the patterns were saturated by spraying with a 1% solution of thioglycollic acid, adjusted to pH 7 with ammonia, folded in two, and then pressed for 15 sec. in the Hoffman press [5].

TESTING PROCEDURE

Angle of Crease

Each strip was immersed in an aqueous solution of Teepol (0·3%) for 3 hr. at room temperature, rinsed in three changes of tap water, and conditioned in an atmosphere at 65% R.H. and 22·2°C. During conditioning, the strip was suspended from one 1¼ in. edge, so that it dried in complete absence of tension, apart from the restraint imposed by its own weight. The angle of the resulting crease was finally measured with the Shirley Combined Stiffness and Creasing Tester, Model 3. For this purpose a length 1 in. × 2 in. was cut from the strip with the crease half-way along the length; one arm was gripped nearly up the crease and the instrument was then adjusted so that the other arm hung vertically. A second measurement was afterwards made with the arms reversed. The second strip was examined in the same way and the four values for the angle of crease were averaged.

Strength and Resistance to Wear

In order to discover whether the fabrics were damaged by any of the above treatments, 13 in. × 2½ in. strips were frayed down to a width of 2 in., treated with the reagents under the conditions already described, and then steamed flat for 15 sec. in the Hoffman press. Only fabrics wetted with either water or the reagent were pressed, and strength measurements were made after the strips had been conditioned at 65% R.H. and 22·2°C. A Denison T42 machine was used, the 2 in. strips being tested with a length of 8 in. between the jaws. Five tests were made on the warp and weft of each fabric.

The resistance to wear of similarly treated fabrics was examined with the Martindale instrument, a standard crossbred (tie-lining) fabric being used as abrasive. The load on the sample under test was adjusted to suit its nature, and the crossbred fabric was changed every 10,000 rubs. Four tests were carried out on each fabric, and the resistance to wear was estimated by determining the change in the conditioned weights of the samples.

RESULTS

The results obtained in the tests are given in Tables II–V.

TABLE II

Angle of Crease

(Fabrics treated with bisulphite solution, rinsed, dried at a low temperature, and then steamed)

Fabric No.	Temp. of Treatment (°C.)	Time of Steaming (sec.)	Angle of Crease of Fabrics treated with Bisulphite Solutions of Concentrations (%)— Untreated	1	2	3	4	5
1	20	5	149	111	93	100	96	94
		15	140	100	89	97	89	91
		15 (wet)	124	91	80	83	86	83
		60	130	92	88	94	83	84
		60 (wet)	100	88	88	69	74	71
	40	5	149	121	122	120	114	109
		15	140	107	116	116	114	109
		15 (wet)	124	105	99	110	105	94
		60	130	102	116	118	110	109
		60 (wet)	100	96	96	105	96	92

TABLE II—*continued*

Fabric No.	Temp. of Treatment (°c.)	Time of Steaming (sec.)	Angle of Crease of Fabrics treated with Bisulphite Solutions of Concentrations (%)—					
			Untreated	1	2	3	4	5
2	20	5	—	105	112	104	106	107
		15	—	99	103	102	99	93
		15 (wet)	120	94	84	95	88	88
		60	126	95	85	91	87	80
		60 (wet)	104	85	79	88	85	76
	40	5	—	126	111	110	116	116
		15	—	108	109	97	101	94
		15 (wet)	120	98	86	95	103	99
		60	126	97	99	103	102	100
		60 (wet)	104	96	90	93	93	99
3	20	5	125	106	100	96	92	92
		15	137	103	93	86	88	81
		15 (wet)	110	81	84	81	82	81
		60	116	97	79	83	78	78
		60 (wet)	102	76	73	70	70	74
	40	5	125	101	98	91	106	90
		15	137	98	—	87	91	88
		15 (wet)	110	98	88	97	86	86
		60	116	90	91	96	87	83
		60 (wet)	102	94	85	86	82	85
4	20	5	—	114	112	109	106	106
		15	134	112	104	106	97	99
		15 (wet)	118	102	94	97	89	89
		60	105	95	98	91	93	91
		60 (wet)	107	83	84	88	82	81
	40	5	—	107	105	103	101	102
		15	134	107	103	101	100	102
		15 (wet)	118	91	94	95	92	91
		60	105	92	97	95	97	95
		60 (wet)	107	90	92	94	94	87
5	20	5	—	102	103	104	105	108
		15	—	101	103	103	101	95
		15 (wet)	117	94	99	85	90	78
		60	117	93	91	80	101	90
		60 (wet)	117	75	80	81	80	72
	40	5	—	107	104	97	107	100
		15	—	107	104	99	94	101
		15 (wet)	117	105	103	94	96	98
		60	117	109	103	99	90	95
		60 (wet)	117	99	98	93	90	91
6	20	5	—	130	119	112	116	117
		15	—	118	120	110	112	113
		15 (wet)	—	108	92	95	97	102
		60	—	116	92	98	101	97
		60 (wet)	125	97	88	81	90	92
	40	5	—	120	116	119	116	117
		15	—	111	112	113	111	113
		15 (wet)	—	110	102	105	107	99
		60	—	102	105	106	95	95
		60 (wet)	125	90	94	98	95	89
7	20	5	—	119	110	110	106	106
		15	—	117	109	108	104	103
		15 (wet)	130	92	95	94	90	93
		60	—	99	100	99	101	98
		60 (wet)	120	84	87	88	89	90
	40	5	—	118	112	105	108	103
		15	—	107	109	100	104	103
		15 (wet)	130	105	94	92	94	99
		60	—	106	104	103	98	98
		60 (wet)	120	95	90	92	88	86

TABLE III

Angle of Crease

(Fabrics impregnated with a solution of sodium bisulphite or ammonium thioglycollate and steamed without rinsing)

Fabric No.	Angle of Crease: Concentration of Bisulphite (%) 0·25	0·50	1·0	2·0	Concentration of Thioglycollate (%) 1	2
1	101	88	78	66	83	—
2	96	84	77	69	89	—
3	75	72	61	64	78	—
4	91	88	83	75	—	83
5	86	84	83	83	—	90
6	114	111	110	100	—	103
7	96	89	87	84	—	89

Discussion

When fabrics are treated with a solution of sodium bisulphite, rinsed, and then dried at a low temperature, the sharpness of the crease obtained by subsequent steaming in the Hoffman press increases with increasing concentration of sodium bisulphite in all the cases examined (Table II). Little advantage is, however, to be gained by increasing the concentration above 2%, and better results are obtained by treating the fabrics at 20°c. than at 40°c.

Comparison of the angles of crease obtained by pressing the air-dry and wetted-out fabrics for the same times (15 or 60 sec.) reveals the great advantage to be gained by damping the fabrics before pressing. Although the longer time of steaming gives a sharper crease in almost all cases, highly satisfactory results are obtained in 15 sec., which is probably as long a time as could be permitted by the large-scale clothier. When bisulphite pretreatment is used, the optimum conditions for obtaining permanent creases in all-wool fabrics may, therefore, be summarised as follows. Treat with a 2% solution of sodium bisulphite for 15 min. at room temperature (20°c.), rinse, dry at a low temperature, and afterwards wet out the fabric, or place it between damp cloths, and press for 15 sec. in the Hoffman press. With fabrics treated under these conditions, the angle of crease retained after 3 hr. immersion in a solution of Teepol (0·3%) at room temperature ranges from 80° for a light-weight tropical suiting to 99° for a grey flannel.

Even better results are obtained if, instead of pretreating the fabrics with sodium bisulphite solution, they are merely impregnated with a dilute solution of sodium (or other) bisulphite before pressing for 15 sec. in the Hoffman press[6]. When

TABLE IV

Tensile Strength of Treated Fabrics

Fabric No.		No Reagent	Tensile Strength (lb.) after using— 3% $NaHSO_3$ (rinsed)	2% $NaHSO_3$ (rinsed)	1·0% $NaHSO_3$ (unrinsed)	0·5% $NaHSO_3$ (unrinsed)	1% Thioglycollate
1	Warp	53·5	58·6†	58·8*	58·9	58·5†	55·0
	Weft	43·0	56·2†	54·4†	49·7	50·4	48·0
2	Warp	83·5	87·9*	91·0†	84·4	83·4	77·6
	Weft	72·4	86·0*	83·2*	78·6†	75·9	75·7
3	Warp	120·0	116·8	119·2	117·8	115·8	111·3
	Weft	113·3	106·8†	106·4*	107·8	103·8*	100·8*
4	Warp	133·3	136·0	136·5	133·5	133·5	128·3†
	Weft	104·8	96·8	97·4	103·8	96·8	98·4
5	Warp	54·4	50·4†	50·4*	49·2*	49·4†	55·2
	Weft	44·8	45·6	44·2	44·2	43·2	44·4
7	Warp	93·2	88·8*	88·2	87·4*	85·5*	85·0*
	Weft	83·3	75·0*	76·6*	77·1*	74·3*	74·2*

* Significantly different from untreated fabric at 1% level

† Significantly different from untreated fabric at 5% level

TABLE V

Resistance to Abrasion of Treated Fabrics

Fabric No.	No Reagent	Loss in Weight (%) of Fabrics treated with— 3% $NaHSO_3$ (rinsed)	2% $NaHSO_3$ (rinsed)	1% $NaHSO_3$ (unrinsed)	0·5% $NaHSO_3$ (unrinsed)	1% Thioglycollate
1	4·04	6·27*	5·60†	6·43*	4·73	5·20†
2	3·37	4·80	5·76*	5·14†	4·63	4·70
3	3·48	3·38	3·93	4·40*	3·62	4·38†
4	1·60	2·45*	2·35†	3·00*	2·90*	2·94*
5	8·95	10·40	8·97	10·82*	9·60	10·05*
6	5·78	6·00	6·05	6·27	5·78	7·90†
7	4·10	5·50†	4·83†	4·67	4·33	4·87†

* Significantly different from untreated fabric at 1% level

† Significantly different from untreated fabric at 5% level

Fabrics 1–4 were tested under the same load, which was greater than that used with fabrics 5–7.

a 1% solution of sodium bisulphite is used, the angle of crease remaining after immersion in the Teepol solution is considerably smaller (i.e. better) for all fabrics except the duvetyn (No. 6) than in the case of fabrics pretreated with the 2% solution of sodium bisulphite, as is seen by comparing the results of Tables II and III. The results of Table III show also that when fabrics are impregnated with solutions of setting agents before pressing, sodium bisulphite gives much sharper creases than ammonium thioglycollate in corresponding concentrations (1% or 2%).

Although impregnation with bisulphite solution immediately before pressing gives the best creases in all-wool fabrics, pretreatment with bisulphite, followed by rinsing and drying at a low temperature, is preferred for commercial use because it allows the cloth to be prepared by the finisher, leaving only the task of pressing to the tailor. The process has the further advantage that, since the whole fabric is treated with the setting agent, there are no differences of shade between, say, coat and trousers, even though the latter have been given permanent creases. Preference for the pretreatment process is reinforced by the data of Table IV, which show that fabrics treated with the 2% solution of bisulphite, rinsed, dried and pressed are stronger than corresponding fabrics pressed after impregnation with a solution of sodium bisulphite or ammonium thioglycollate. In general, also, fabrics pretreated with the 2% solution of bisulphite have a greater resistance to abrasion than those pressed after impregnation with the setting agent, though all methods of pressing cause a fall in wear-resistance, as shown in Table V.

* * *

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The Pad-Roll Dyeing System. A Summary of Experience

R. KERN

The results obtained in practical trials with the Pad-Roll dyeing system are described. Fabrics composed of cellulosic, polyamide, polyester and acetate fibres have been dyed with direct and disperse dyes, and some trials have been made with acrylic fibres and wool, as well as with blended fibre fabrics. Methods for overcoming some practical difficulties are described.

INTRODUCTION

The Pad-Roll machine, manufactured by A/B Svetema of Gothenburg, Sweden, is no longer a new development. The first unit was installed some five years ago and there are now 60 or more in operation in various parts of the world. The firm is also building a bleaching range on similar principles but of slightly different construction.

It has long been known that cellulosic materials can be dyed by impregnation with an aqueous, preferably hot, dye liquor; the goods are then beamed and wrapped in waterproof cloth. When left in this state for a sufficiently long time (24 hr. or more) the dye is fixed on the fibre. Although used in some dyeworks, this method has been of little practical significance because of its excessive demands on time and working space. Its basic principle is dyeing with an extremely short liquor: goods ratio, generally 1 : 1.

The Pad-Roll machine works on the same principle, with provision for exact control of dyeing conditions. It consists of three components— the pad and the infrared heating zone, both fixed units, and the "dyeing-in" chamber or chambers which are movable and exchangeable. Complete details of the machines have already been given [1, 2], and the purpose of this paper is to describe practical experience in works and laboratory of the use of the dyeing system with various types of fibres.

CELLULOSIC FIBRES

Before dyeing, cotton, viscose rayon and cuprammonium (Bemberg) rayon must be thoroughly prepared by desizing and scouring, followed by bleaching where required by the quality of the goods and the colour to be dyed. Contrary to a widely held view, the goods must be more thoroughly and carefully prepared for padding than for conventional dyeing. This should be obvious, for after passing through the pad the dye has no further opportunity to migrate and cover irregularities in the fabric.

Wherever possible, pretreatment should be carried out in open-width. Quite often goods scoured on the winch in rope form are left with creases or folds and abrasion marks which are not visible in the dry state but show up after dyeing, because dye absorption is usually higher in such places and is not corrected by migration during the dyeing-in period. There are certain fabrics, especially those of light-weight construction, which can be pretreated in rope form and dyed satisfactorily, but even here the possibility of fibre damage should be carefully investigated before dyeing in bulk.

The object of these pretreatments is to give the goods the highest possible absorptive capacity, a factor of decisive importance in pad dyeing. Desizing is also advisable when water-soluble sizes

are present, because they are not always removed evenly and completely, which again can lead to substantivity differences. If goods treated with a water-soluble size are padded in this state, size will accumulate in the liquor and similar difficulty will be experienced. Uniform scouring contributes a great deal to good dyeing, and should be carried out with only slight tension if possible. Whether bleaching is necessary or not depends on the colour required and the type of fabric; it is probably essential with very bright pale colours. Goods which do not show the desired absorptivity after desizing and scouring often become more absorbent after bleaching.

After the pretreatments the goods must be dried in open-width under minimum tension. Overdrying must be avoided at all costs, because the goods then absorb atmospheric moisture unevenly while awaiting dyeing, and this will lead to uneven uptake of padding liquor. This is especially likely to happen with overdried goods when they are beamed or folded down in a truck, the outside and selvedges of the roll or the top layer of fabric then being free to absorb moisture more quickly than the rest of the piece. Differences of only 5–10% in moisture content can lead in ending or tailing in Pad–Roll dyeing. Temperature differences in the fabric itself, i.e. at the outer end of a beamed length, cause the same faults. A good safeguard against uneven moisture uptake is to lead the fabric over cooling drums on leaving the drier. Tension in the drier must be kept to a minimum, so that the goods do not shrink unduly when padded, which gives rise to differences in tension that can influence the depth of shade.

If there are no cooling drums available, it is advisable to heat the goods before they enter the pad, either on heating drums or in a short infrared zone. The purpose of cooling, after drying or heating before padding, is to ensure that the goods are of uniform absorptivity and moisture content. In the interval between drying and padding they should be stored where they are safe from inadvertent spotting with water and impurities. Water drops can penetrate several thicknesses of cloth, and the spots are dyed much lighter, sometimes being left white. Impurities, especially when of a fatty nature, lead to similar faults which make the goods unusable. The storage room should be one where the goods are not exposed to abnormal humidity conditions.

In principle, all the pieces making up a batch should be pretreated and dried at the same time. This alone ensures that the absorptive capacity and uptake of dye will be constant. If pieces which have not been pretreated at the same time are sewn together and dyed as a batch, one of them may be dyed weaker or heavier than the others.

The pieces should be sewn together with a normal straight stitch so that they run straight and even. The seam should be as narrow as possible; broad seams absorb too much liquor and are dyed deeper, and, in addition, they press through several thicknesses of cloth, producing bars, so that a considerable length at the ends of the pieces must be discarded. Strong thread should be used to prevent breakages and hold-ups in production, but it should not be too elastic, because, when the goods are under tension in the pad, adjoining pieces are apt to be pulled apart, and when the tension is relaxed they will be drawn together and overlap. In practice, sewing yarns as similar as possible to the material have been found to give the best results.

There are various opinions as to the most suitable end-cloths. Preferably they should be of the same material as the goods to be dyed, but the cost is often prohibitive. In some dyeworks cloths of acrylic fibre have given good service; they can be easily washed clean (when used with cellulosic fabrics) and can be constantly re-used. The end-cloths should not be narrower than the goods—usually they are wider—and must be absolutely flat in the open and the beamed state, because creases and wrinkles are likely to cause darker places in the dyed goods.

In padding, an attempt must be made to work with the smallest possible volume of liquor, in order to obtain a rapid rate of bath renewal and to minimise affinity differences between the different dyes. The volume chosen depends chiefly on the absorption and wetting properties of the cloth. Wetting agents should not be used because foam has an adverse effect on level dyeing. The liquor level should remain as far as possible constant, so that there are no variations in the uptake of dye, as this again can lead to differences of depth. The temperatures should also be constant. Both these factors are controllable on the Pad–Roll machine. When direct cotton dyes are used, the concentrated brands should be chosen, except in a few cases. Practical experience has shown that a small addition of Glauber's salt or sodium pyrophosphate (up to 5 g./litre) has a beneficial effect on fixation.

With the Svetema pad of the Pad–Roll machine there is little danger of the liquor running back on to the cloth. If other padders are used, care must be taken to avoid this effect, as otherwise two-sidedness is likely to occur. The feeding liquor should not be led into the pad in such a way that it comes into contact with one side of the fabric only, because this too can lead to two-sidedness. Loose fibres adhering to the rollers must be removed with a brush or other means so as to prevent spotting.

The expression should be as nearly as possible 100%. This is not always feasible, but with cellulosic fibres an increase of less than 80–85% over the dry weight should be avoided. Inadequate uptake does not give the dye sufficient liquid for complete fixation and may result in a dull shade.

The goods may also absorb additional moisture from the atmosphere in the dyeing-in chamber, and where this happens the fixation will be better. Moisture uptake in the rolled state is naturally greatest at the selvedges and the outside, which can likewise lead to unlevelness. Laboratory trials have shown that if the nip pressure is too high the goods may be two-sided; it is best to work with an expression (pick-up) of 90–95%.

Dyes should not be applied at concentrations close to their maximum solubility. At very high

concentrations a portion of the dye may remain undissolved and be attached to the cloth in this form. It is also possible that dyes in combination may interact and so cause precipitation, but this phenomenon has not yet been observed in practice. The solubility is improved by adding 100 g./litre of urea or Lyogen TG, neither of which has an adverse effect on fixation.

At high dye concentrations it is advisable to pad at the highest permissible temperature in order to keep the dye in solution and to heat the goods. It is possible that the fabric may cool between the pad and the heating zone, causing the dye to precipitate, and, although the fabric is again heated in the zone, it is not absolutely certain that precipitated dye will redissolve. It was formerly maintained that oversaturated dye liquors, i.e. liquors containing undissolved dye, could be used, but experiments have shown that in most cases the results are inferior and the colour fastness below the proper standard.

The dyes chosen for combination shades should have similar affinities at the padding temperature. For this purpose the exhaustion curves shown in pattern cards serve as an approximate guide; they are necessarily approximate, since they refer to standard-strength dyes and not to the concentrated brands. The affinity in padding does not appear to be exactly the same as in exhaustion dyeing. No successful method of measuring substantivity in the padder has yet been devised owing to the technical difficulties involved, so practical experience must be applied to solve the problem.

A tension-adjusting device with a jig roller is fitted between the pad and the infrared zone. The roller is provided with an electrical contact which regulates the winding speed of the drum in the dyeing-in chamber so that the cloth remains under constant tension in spite of the increasing diameter of the roll. The tension is adjusted from the control panel; it must be as low as possible and should remain very nearly constant throughout the padding process. Variations of tension can lead to unlevelness and two-sided effects, particularly with viscose staple fabrics, which are apt to shrink in the dyeing-in chamber; if wound too tightly in the first place the tension will become excessive.

After passing through the tension adjuster the padded goods enter the heating zone where both the dye liquor and the cloth are heated to a temperature as near as possible to that of the dyeing-in chamber. Correct operation of the heating zone is of the utmost importance. Overheating may lead to premature drying, with correspondingly poorer fixation. Moreover, water vapour may then accumulate in the slot of the chamber and, after condensation, drip on to the goods entering the chamber. Unless the dyes exhibit very good migration, the spots caused by dripping water will be left white on fixation. The entrance slot is heated, but, when heating in the infrared zone is excessive, dripping cannot be prevented. If on the other hand the zone is not sufficiently heated, the dyeing-in temperature falls and the goods require longer for fixation. The heating is controlled by hand and no general rules can be made; the correct control of heating depends on the colour and on the fabric and can only be learned from experience.

In the dyeing-in chamber there are guide rolls in front of the drum to ensure that the fabric is wound straight. The last and largest of these is mounted on arms and can be moved towards and away from the drum by means of a hand-wheel. Generally it is moved close to the drum, but it should not transmit too much tension to the fabric. It is extremely important that the selvedges should run straight, otherwise they may be dyed unlevel. If a selvedge is folded during padding it should be straightened immediately with small wood or plastic clips, which can be left in the roll as they do not interfere with the dyeing. Creases must be avoided, because they are dyed darker and press on adjacent parts of the fabric, causing further dyeing faults. Goods which are free from weaving faults and have been suitably pretreated, dried with minimum tension and sewn together correctly do not generally form creases. Creasing often occurs with fabric that is not wound perfectly straight and leads to faults which make stripping necessary.

The dyeing-in chamber is equipped with an electrical heating device and a steam inlet valve, both of which are automatically controlled, and a wet- and dry-bulb thermometer. The dry thermometer regulates the heating, and the wet thermometer the steam. When the chamber is loaded and moved out of line the steam supply must be regulated by hand. Both temperatures should remain as far as possible constant, with the dry temperature invariably higher than the wet. If the wet temperature equals or exceeds the dry temperature, atmospheric moisture will condense and drip on to the goods, causing spots. Conversely, if the wet temperature is too low in relation to the dry, the material may become dry, thus causing the same faults. The wet temperature should not normally be more than 10°C. lower than the dry temperature; the best results have been obtained with a difference of about 5°C. With cellulosic fabrics the best results are obtained with dry temperatures of about 85°C. and wet temperatures of about 80°C., but lower temperatures and greater differences are sometimes recommended.

Exact temperature control is most difficult during padding, because hot, damp material is entering the chamber continuously. The automatic temperature controls should perform this function, but practical trials have shown that the wet thermometer does not usually regulate the steam supply rapidly enough. Usually too much steam is introduced, so that with the additional moisture in the goods and the heat transmitted in the infrared zone the wet temperature begins to rise. Very often better results are obtained when the steam supply is controlled by hand. The automatic control of the dry temperature is generally satisfactory.

It is important that the chamber should be properly heated and have the necessary moisture content before dyeing is started; this can be checked with the two thermometers. The most

successful results have been obtained when the two temperatures remained constant for at least 15 min. A constant dyeing-in temperature is maintained by control of heating and of the steam supply. The more constant the temperature, the greater the probability of successful dyeing.

The dyeing-in time depends largely on the depth of dyeing and the type of fabric. Light colours and light-weight fabrics require less time for fixation, usually about 3 hr., whilst heavier depths generally need 4–5 hr., or up to 8 hr. for navy blues and blacks. These are of course only approximate figures, for the fixation times of the dyes used can differ markedly.

When the loaded dyeing-in chamber is removed from the range, it is next connected to electric power and a steam supply, and the drum is rotated slowly by a small motor. The steam charge is controlled by hand and must be checked regularly. Usually little steam is needed to maintain constant humidity. During dyeing-in, the wet and dry temperatures must be constant to within ± 2°C.

After fixation, it has been found advantageous to allow the goods a short air passage using, e.g. a roller set level with the chamber.

Light and medium colours do not usually require rinsing because the dye is completely fixed. Heavier depths must be rinsed, as they are likely to contain unfixed surface dye. Even with lighter colours it is advisable to lead the cloth through a cold-water bath, e.g. in a pad trough. For heavy depths open-width washers are more convenient.

Aftercoppering dyes, when applied for pale depths, can be coppered on the pad. The concentration of the aftercoppering bath is calculated on the moisture content of the goods and the expression, in order to ensure that sufficient copper is applied. If coppering is carried out on a padder it is advisable to follow it with an air passage of about 10 sec. If this is not possible the cloth should be rolled up and stored for some time. Aftercoppering baths must be heated to 50–60°C. Coppering can also be done in an open-width washer or other suitable equipment. If an open-width washer with sufficient boxes is used, the coppering bath can follow rinsing, but in all cases a further rinse after coppering is desirable. With small batches, several different shades can be dyed-in in a single chamber, provided that sufficiently long end-cloths are used to separate the colours and prevent staining. Wherever possible, pieces which are dyed-in together in this way should be of the same material and width. Fabrics of different fibres create difficulty in tension control and fabrics of different widths press down the selvedges.

The Pad–Roll machine has been successfully used for dyeing a wide variety of fabrics. It is difficult to dye thick fabrics satisfactorily because of the pressure exerted by the pad and the tension on the drum, but sateens have been dyed without showing a moiré effect. Thanks to the excellent penetration, weaving faults such as warp and weft stripiness can usually be covered, an advantage which is specially appreciated with linings.

HYDROPHOBIC FIBRES

Although originally designed for dyeing cellulosic fibres, the Pad–Roll system has latterly been used with success for polyamide, polyester and acetate rayon cloths. Because of their hydrophobic character these materials are padded in presence of thickening agents, the most suitable being alginates and crystal (industrial) gum. Despite the low absorptivity, careful preparation is necessary in order to remove all impurities, especially those of a fatty nature. Pretreatment is best carried out in open width, taking special care to ensure even drying.

The amount of thickening used depends mainly on the construction of the fabric; smooth, tightly woven cloths require more than loosely woven staple fibre fabrics, but the padding liquor must be thin enough for the feeding liquor to flow freely. The maximum amounts of thickening agent commonly used are 3–5 g./litre for alginates and about 50 g./litre for crystal gum. These are only approximate figures, for different commercial qualities vary considerably in viscosity.

Foaming is particularly objectionable with hydrophobic fibres, as it gives rise to inferior dyeings, especially in the case of tight, smooth materials. Supernatent foam is deposited by the fabric on the pad rolls, and from there small bubbles are sometimes left on the cloth. In the heating zone the bubbles burst, forming small rings which are usually dyed deeper. These faults are rarely corrected in the dyeing-in chamber. The foam-inhibitor Antifoam B (Dow Chemicals) has given excellent service; it is based on silicon, is economical in use and appears to have no adverse effect on dyeing. It is probable that the static electricity which is often present in these fabrics contributes to foaming. In some dyeing trials with acetate rayon and nylon, the electrostatic charge generated during unwinding was so powerful that the hair of persons standing nearby stood on end. Static electricity attracts dust, and goods soiled in this way may easily show dyeing faults. Antistatic treatment of the material would undoubtedly be advantageous.

The uptake of padding liquor by hydrophobic fibres varies with the fabric construction. Generally it lies between 30% and 50%, and in rare cases approaches 60%, as compared with 80–100% with cellulosic fibres. This creates special problems when dyeing with water-soluble dyes, as high solubility is required for the production of heavy depths. The following example illustrates this point.

A 5% dyeing on nylon was required. The maximum obtainable expression was 30%, so the dye concentration of the liquor had to be 166 g. per litre (at 100% expression only 50 g. dye per litre would have been necessary). With disperse dyes solubility is no problem, but pasting and dispersion is more difficult at such high concentrations.

The padding liquors must be carefully prepared. Water-soluble dyes should be dissolved alone and the solution filtered before the thickening and the acid-yielding agent are added. Artisil ultra-dispersed dyes should be pasted and dispersed with cold water only. When a satisfactory dispersion

has been obtained, it should be strained through a sieve or filter cloth before the thickening is added in order to eliminate coarse particles which inevitably lead to spotting. It is best to prepare a stock solution of the alginate thickening. This too should be filtered before being added to the dispersion, for it may contain small, almost invisible alginate nodules which are crushed by the pad rolls and produce lighter coloured or white spots on the fabric.

"Ultra-dispersion" was originally used for the Sandothrene vat dyes. When it was later applied to the Artisil disperse dyes it was assumed that this range too was equally suitable for padding, although the ultra-dispersed form was in fact developed for exhaustion dyeing to overcome certain recurring difficulties encountered with the ordinary brands. For this reason no special measures were taken to ensure uniformity of particle size, because in dyeing, occasional coarser particles do not cause spotting as they do in padding. It is therefore advisable to filter Artisil dispersions carefully before they are added to the padding liquor.

Secondary Acetate and Triacetate Rayon

These fibres can be padded at 40–60°c. on the Pad–Roll machine with ultra-dispersed Artisil dyes in presence of a thickening agent. The dyeing-in times are 3–5 hr., depending on the depth. For fabrics consisting of 100% secondary cellulose acetate a dry temperature of 80°c. is sufficient, but it can be increased to 85°c. or more for blends with other fibres. For triacetate rayon higher temperatures should be chosen, e.g. at least 90–95°c., and in some cases longer dyeing-in times are necessary. With blended fabrics the padding temperatures can be increased if the solubility of the other dyes used is thereby improved.

Nylon

With Artisil dyes the dyeing conditions are the same as for acetate fibres, but generally the temperature should be slightly higher than for 100% secondary acetate.

With acid dyes nylon fabrics showing pronounced barriness cannot be dyed level on the Pad–Roll machine, except by means of special methods. If the tendency to barriness is only slight the results may be satisfactory.

A method has been developed for the level dyeing of barry polyamide fibres using Lyogen P; it has been adapted to the Pad–Roll system and gives very good results. The goods are pretreated with 2 g. Lyogen P and 2 g. acetic acid (40%), per litre. Starting at 50°c., the bath is brought to the boil in 20 min. and boiled for 30 min. The goods are rinsed with cold water until neutral and then dried. If the material is not unduly soiled this treatment should also serve for scouring. If separate scouring is necessary it should be carried out before the Lyogen P treatment.

The dyes recommended for the Lyogen P dyeing method should also be used for padding. The liquor should contain 5 g. ammonium sulphate per litre and a suitable thickener, but no further Lyogen P. The dyeing-in time is 2–5 hr., depending on the depth, at a dry temperature of 90–95°c., and dyeing is followed by thorough rinsing. Aftertreatment with tannic acid and tartar emetic is recommended to improve the wet fastness properties; it is essential when cationic finishing agents are applied later.

Polyester Fibres

Pad–Roll dyeing trials with Artisil dyes on polyester fibres commenced only recently, but laboratory and practical work has shown that the highest attainable temperatures must be employed to achieve success. In the dyeing-in chamber the wet temperature must be 95–100°c. and the dry 105–110°c. Although it is not easy to maintain these high temperatures and the required moisture content, considerable yardages of cloth consisting of 100% polyester fibres and of polyester fibre blends have been dyed by the Pad–Roll method. The preparation of the goods and the composition of the liquor are the same as for dyeing nylon with disperse dyes. It is best to use Foron dyes and those Artisil brands suitable for dyeing polyester fibres. A carrier is usually necessary for heavy depths, but not for light and medium colours.

Although the trials are not yet complete, the results obtained so far suggest that *o*-phenylphenol is the most suitable carrier, but owing to its detrimental effect on light fastness, it must be removed by subsequent heat treatment. About 5 g. *o*-phenylphenol per litre of padding liquor is required, or about 2·5 g. of Dilatin TC.

The dyeing-in times are much longer, e.g. up to 6 hr. may be necessary. Aftertreatment at the boil with a detergent, e.g. Sandopan WP, and 3 g. soda ash per litre is advisable in order to remove all traces of unfixed dye; this is especially recommended in the case of heavy depths.

Acrylic Fibres

Very few trials have been made with these fibres. They can probably be dyed successfully to light or medium depths with disperse dyes. Basic dyes have not yet been tested.

WOOL

Attempts to dye wool on the Pad–Roll machine have been disappointing. The poor wetting properties of wool make it difficult to impregnate properly, and projecting fibres are not dyed satisfactorily. Sandopan DTC is a suitable wetting agent. The fixation is good and it is possible that very smooth fabrics can be dyed successfully.

BLENDED FABRICS

The Pad–Roll machine is very suitable for dyeing blended fabrics. The padding liquors are prepared with the dyes and other additions for the two different fibres, the dyeing-in conditions being determined by the fibre which requires the longest time and highest temperature for fixation.

CONCLUSIONS

The Pad–Roll dyeing system has a wide field of use which should increase in course of time. The machine is commercially interesting only for long yardages. For many commission dyers the adaptation of laboratory recipes to batch dyeing is

one of the major difficulties, since the small laboratory Pad–Roll unit by no means simulates the large machine. However, it should be possible for the engineers to build a padder which will make it possible to formulate more readily transferrable recipes.

Printers have discovered that material dyed by the Pad–Roll method is not easily dischargeable to a good white. This is due to the greater penetration, as compared with normal exhaustion dyeings. It has also been found that impurities in the dye are absorbed by the fibre and can contribute to the poorer dischargeability.

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The Solubilities and Heats of Solution of Disperse Dyes in Water

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The aqueous solubilities of 16 carefully purified disperse dyes have been measured over the temperature range 60–90°C. From these results, the heats of solution in water have been found to lie mainly in the range 10–20 kcal./mole. It is suggested that the higher heats of solution are associated with the presence of hydroxyl groups in the dye molecules, and the possibility of intermolecular hydrogen bonding in the crystalline state. Values for the melting points, wavelengths of maximum absorption and molar extinction coefficients are also given.

INTRODUCTION

The dyeing of polyester fibres such as Terylene appears to have a number of features in common with that of cellulose acetate. In particular, both may be dyed with the same class of dyes, viz. the disperse dyes. There is evidence of some correlation between the aqueous solubility of the latter and the dyeing behaviour of these fibres[1, 2]. It was thus considered important in a fundamental study of the dyeing of polyester fibres[3] to have more comprehensive data on the aqueous solubility characteristics of disperse dyes.

When the work described in this paper was begun, little information on this topic was available, apart from some values of solubilities at 25° and 80°C.[1]. Later, however, results were published giving more extensive affinity data, together with heats of aqueous solution[4]. Thus it is inevitable that some of the measurements were duplicated, but they form a basis for useful comparison.

In the present work the dyes have been further characterised by means of light-absorption curves in aqueous acetone, from which molar extinction coefficients have been calculated.

EXPERIMENTAL

Purification of Dyes

Most of the dyes were obtainable in paste form free from added diluent, etc., but were nevertheless subjected to a severe purification treatment. This consisted of recrystallisation in turn from chlorobenzene, Cellosolve, and benzene. Each stage was monitored by melting-point measurements using N.P.L. calibrated thermometers, and by chromatographic assessment. A dye was used only when it appeared pure, as judged by constancy of melting point and production of a single spot on the chromatogram. The chromatography was carried out on a Whatman No. 1 paper support from acetone solution, using chlorobenzene or petroleum ether saturated with methanol[5] as eluent.

Measurement of Solubilities

The method used was similar to that used by Bird, Manchester, and Harris[6]. After purification and drying at 70°C., the solubility of each dye was measured in duplicate at four temperatures, the control being within ± 0·1°C., even at the highest temperature used.

Purified crystalline dye (200 mg.) and distilled water (50 ml.) were placed in 2 oz. bottles fitted with rubber bungs. The bottles were gently agitated by a crank during the experiment and were almost completely immersed in the thermostat bath at 60°C. As was found by previous workers[6], it required three days for the solutions to become saturated. After this time samples of the solution were taken with a pipette fitted with a No. 2 sintered-glass filter to exclude solid dye particles. The pipette was kept in a sheath immersed in the thermostat tank, so that no dye was deposited due to cooling when the pipette was filled.

The sample of the dye solution was quickly transferred to a tared 25 ml. flask containing 12·5 ml. of acetone. The flask was then cooled, reweighed in order to determine the exact weight of dye solution taken and made up to 25 ml. with water. The optical density at the wavelength of maximum absorption of visible light was then measured with a Unicam SP500 spectrophotometer. The concentration of dye in the sample was calculated using extinction coefficients previously determined with standard solutions of the dye. The temperature of the thermostat was then raised to 70°C. and, after three days, further samples were taken. The same procedure was followed at 80°C. and 90°C.

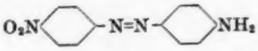
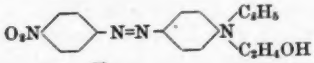
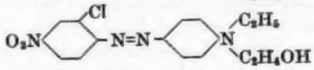
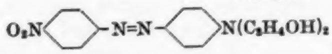
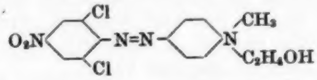
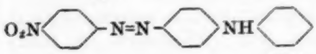
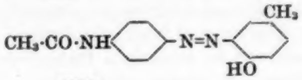
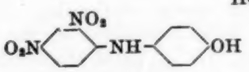
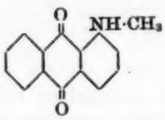
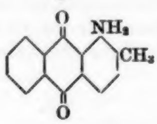
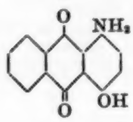
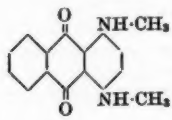
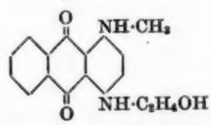
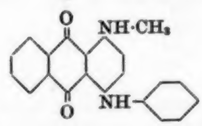
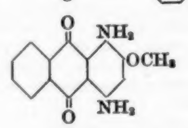
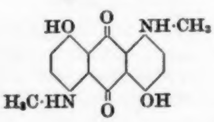
There was no apparent decomposition of the dyes at these temperatures, but it was later found that at least one dye (C.I. Disperse Orange 5) began to decompose after four days in water at 100°C.[7]

RESULTS

Table I shows the chemical structures, melting points, wavelengths of absorption maxima (λ_{max})

Table I

The Properties of some purified Disperse Dyes

C.I. Disperse	Chemical Constitution	M.p. (°C.)	Published M.p.[1,8] (°C.)	Wavelength ($m\mu$.) of Absorption Maximum in 50% Aqueous Acetone	Wavelength ($m\mu$.) of Absorption Maximum in Chlorobenzene	Molar Extinction Coefficient (ε) 50% Aqueous Acetone	Molar Extinction Coefficient (ε) Chlorobenzene
Orange 3		215	215, 214	440	420	24,200	25,900
Red 1		165	163, 161	500	480	36,100	29,500
Red 13		133	135·5	520	510	34,850	33,100
Red 19		209	206·5, 205	500	—	33,350	—
Orange 5		127	—	450	440	25,200	22,600
Orange 1		162	158, 157	480	—	31,800	—
Yellow 3		195	196·5	360	—	18,850	—
Yellow 1		194	195	370	360	16,500	14,600
Red 9		161	167, 165	520	—	8,050	—
Orange 11		208	205	480	470	8,050	6,870
Red 15		218	210·5	530	520	10,500	9,800
Blue 14		224	221, 220	590	—	16,200	—
Blue 3		187	—	590	—	16,900	—
Blue 24		151	148	600	—	15,700	—
Red 11		242	241, 240	530	—	17,700	—
Blue 26		217	—	590	600	17,300	15,200

in the visible region of the spectrum, and molar extinction coefficients (ε) in 50% aqueous acetone for the 16 purified disperse dyes. In a number of cases λ_{max} and ε are also given for chlorobenzene solutions, this solvent generally giving lower values. These latter values were required in other studies [3]. Melting points reported by Bird [1] and by Daruwalla and Limaye [8] are also given for comparison.

In Table II the solubilities at 60°, 70°, 80°, and 90°C. are given, together with heats of solution ($\Delta H°_{H_2O}$) calculated from the van't Hoff relationship—

$$\Delta H°_{H_2O} = \boldsymbol{R}\frac{\mathrm{d}\ln S_T}{\mathrm{d}\,(1/T)}$$

where S_T is the solubility (g./litre) in water at T°K. Plots of ln S_T and $1/T$ were made, and $\Delta H°_{H_2O}$ found from the slope of the best straight line through the experimental points. Such published data as are available are also included.

DISCUSSION

The present results confirm the extremely low aqueous solubilities found by Bird and Harris [4], although there are numerical differences in most cases. The solubilities found in the present work are generally lower, but the fact that the melting points are higher suggests that the dyes were purer, rather than that the solutions, despite precautions, were unsaturated. There are only two exceptions (C.I. Disperse Yellows 1 and 3) to the rule that higher solubility coincides with a lower melting point, which will usually be due to the presence of impurity. In view of the very low absolute solubilities, even a small fraction of impurity in the dye which can dissolve in water independently of the major component will effect a considerable increase in the measured solubility, if the light-absorption characteristics of the two are similar. This conclusion is supported by measurements on the solubilities of mixtures of dyes, which were found to dissolve independently.

A comparison of the heats of solution shows also that ours are several kcal. lower, but that C.I. Disperse Yellow 1 is again an exception. This dye is discussed later. It should, however, be remarked that low solubilities measured over a relatively small range of temperatures are not necessarily linked to low heats of solution, since the latter reflect the change of solubility with temperature rather than its absolute value.

By making certain assumptions it is possible to interpret the differences in heats of solution between the various dyes in terms of intermolecular forces. The overall heat of solution, $\Delta H°_{H_2O}$, may be considered to include a term dependent on the separation of water molecules, $\Delta H°_{WW}$ (heat absorbed), a term dependent on the separation of dye molecules, $\Delta H°_{DD}$ (heat absorbed), and a term dependent on the formation of dye–water bonds, $\Delta H°_{DW}$ (heat evolved). Thus we can write—

$$\Delta H°_{H_2O} = \Delta H°_{DD} + \Delta H°_{WW} - \Delta H°_{DW}$$

For the purposes of comparison of different dye molecules of approximately similar size, the second term on the right-hand side of this relationship may be disregarded. Thus the value of the heat

TABLE II

The Solubilities and Heats of Solution of Disperse Dyes in Water

C.I. Disperse	Temp. (°C.)	Solubility (mg./litre)	Temp. (°C.)	Solubility (mg./litre)	Temp. (°C.)	Solubility (mg./litre)	Temp. (°C.)	Solubility (mg./litre)	Heat of Solution (kcal./mole)	Comparison Values [1,4] Heat of Solution (kcal./mole)	Comparison Values [1,4] Solubility at 80°C. (mg./litre)
Orange 3	60·0	3·0 —	69·9	4·8 7·8	80·0	9·2 9·9	90·4	15·5 17·8	13·3	15·4	11·4
✓ Red 1	60·0	1·9 2·2	70·0	3·3 3·5	80·0	5·6 5·8	90·0	10·6 10·7	12·8	17·5	7·7
Red 13	60·6	0·4 0·3	70·0	1·6 1·5	80·5	2·5 4·1	89·0	3·7 4·8	20·6	16·1	4·0
Red 19	60·2	3·8 3·9	70·0	7·2 7·8	81·0	16·3 12·9	90·3	33·0 32·0	16·9	17·6	21
Orange 5*	60·0	3·3 —	69·9	5·4 6·0	80·0	9·8 11·9	90·4	23·3 23·8	16·9	18·3	7·6
Orange 1	60·2	0·0 —	70·0	0·2 0·5	81·0	0·7 1·4	90·3	1·0 1·3	10·1	—	0·5
✓ Yellow 3	60·0	1·5 6·1	69·9	4·4 4·9	80·0	12·0 12·7	90·4	31·6 28·5	23·3	16·3	26·1
Yellow 1	60·2	16·4 17·7	70·0	35·2 49·9	81·0	75·2 87·4	90·3	154 152	16·9	13·3	125
Red 9	60·6	1·7 1·0	70·0	6·4 6·2	80·5	8·2 8·2	89·0	15·4 9·7	10	14·3	6·1
Orange 11	60·6	1·6 4·2	70·0	6·1 7·7	80·5	7·2 8·2	89·0	12·4 13·0	11·4	15·5	8·3
Red 15	60·0	2·6 2·8	70·0	4·1 4·5	80·0	5·4 5·7	90·0	12·8 10·3	12·3	18·4	11·7
Blue 14	60·8	2·8 —	69·8	2·1 —	81·0	2·1 —	92·0	4·8 —	11	—	2
✓ Blue 3	60·2	2·2 1·6	70·0	5·7 4·5	81·0	13·3 12·3	90·3	32·8 26·0	20·6	16·7	30·3
Blue 24	61·6	0·0 —	71·3	0·2 0·4	79·8	0·1 0·1	89·5	0·5 0·7	9	—	< 0·2
Red 11	61·6	6·5 —	71·3	7·2 —	79·8	9·3 12·8	89·5	14·8 15·5	8·2	14·3	16·0
Blue 26	60·0	0·4 0·4	69·9	0·9 0·8	80·0	1·7 1·7	90·4	3·3 3·7	17·4	—	—

* In Ref. 4 this dye is incorrectly described as the "*N*-ethyl" derivative (cf. Table I previous page).

of solution, experimentally found to be positive in all cases, depends upon the difference between the first and third terms. If the nature of the bonds between dye molecules and between dye and water molecules is the same, e.g. hydrogen bonds, then it is probable that the stronger the bonds between molecules in the dye crystal, then the stronger will be the bonds between dye and water in the solution. If we assume further that the heat associated with the formation of dye–water bonds is a *regular* positive function of the strength of intermolecular bonds in the dye crystal, then, although an increase in the heat associated with the separation of dye molecules from each other will mean an increase in the heat associated with the formation of dye–water bonds, it also follows that the difference of the two will be greater. Therefore the measured heats of solution, being positive, may be taken as a measure of the attractive intermolecular forces between dye molecules, and this provides a basis for explaining some of the differences in the heats of solution.

Whilst any division into groups can hardly be more than arbitrary, the seven heats of solution ranging from 23·3 to 16·9 kcal./mole relate to dyes which all possess hydroxyl groups and therefore have the possibility of forming intermolecular hydrogen bonds, whereas the six heats in the lower group, from 11·4 to 8·2 kcal./mole, relate to dyes with no hydroxyl groups. Of the remaining three dyes, only C.I. Disperse Orange 3, with the largest heat of solution, has no hydroxyl groups in its structure. But for this exception, all three dyes could be added to the first group, with a dividing line about 12 kcal./mole separating dyes which possess hydroxyl groups from those that do not. In general, then, it seems that dyes which can form strong intermolecular bonds have the higher heats of solution.

On the other hand, if the dye can form strong intramolecular bonds, depending upon the positions of the substituent groups, then the heats of solution may be lower than at first expected. This may explain the somewhat low value for C.I. Disperse Red 15 (1-amino-4-hydroxyanthraquinone), although attention is drawn to the previously published result of 18·4 kcal./mole for this dye[4], which is higher than found in the present studies.

A further point of interest is the high solubility of C.I. Disperse Yellow 1, which has a mean solubility of 153 mg./litre at 90°C., nearly five times that of the next most soluble dye. C.I. Disperse Yellow 1 is, however, outside the two chemical classes into which all the other dyes fall, being a derivative neither of azobenzene nor of anthraquinone. The hydrogen atom attached to the nitrogen atom between the two benzene rings may alter the polarisability of the hydroxyl group or assist in the formation of bonds in a plane perpendicular to those of the benzene rings. Further work on heats of vaporisation of these dyes would be of assistance in confirming these speculations.

* * *

The experimental work was mainly carried out by Mr. E. Jackson in the Research Department, ICI Ltd., Fibres Division, Harrogate, and we also thank Dr. E. P. Goodings for helpful discussions. Thanks are due to the Research Department, ICI Ltd., Dyestuffs Division, for supplying the samples of dyes.

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(*Received 17th September 1959*)

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[1] Bird, J.S.D.C., **70**, 68 (1954); see also Bird, Partovi, and Tabbron, *ibid.*, **76**, 600 (1960).
[2] Schuler and Remington, *Faraday Society Discussion on Dyeing and Tanning*, (16), 201 (1954).
[3] Patterson and Sheldon, *Trans. Faraday Soc.*, **55**, 1254 (1959).
[4] Bird and Harris, J.S.D.C., **73**, 199 (1957).
[5] Elliot and Tolesz, *ibid.*, **73**, 8 (1957).
[6] Bird, Manchester, and Harris, *Faraday Society Discussion on Dyeing and Tanning*, (16), 85 (1954).
[7] Patterson and Sheldon, Unpublished results.
[8] Daruwalla and Limaye, J.S.D.C., **74**, 464 (1958).

Defective Colour Vision

Comparison of a Colour Vision Test made from Dyed Wool Patterns with the Ishihara Test

J. G. WAIN

The Wain Dichroic-ladder test and the Ishihara test have been used to test 409 males. Of those tested, 9% were found to be defective by the Ishihara test. Statistical analysis of the results obtained from the Wain test showed that a further 3% of the observers could be regarded as having some form of colour defect. The new test was constructed so that it subtended an angle of 10° at the eye. Comparison of the observers' matches with the plots of the predicted matches suggests that the short-wavelength receptors of the retina extend at least up to the boundary of the 10° field.

INTRODUCTION

The construction of the Wain Dichroic-ladder test from wool patterns has been described recently[1]. The test consists of four separate ranges of dyed wool patterns each of which has to be matched by a "floater", i.e. a single pattern prepared from dyes which change hue when viewed in tungsten light, compared with daylight. The matchings were made under a Siemens colour-matching unit FTF 2444. Tests were carried out, by the same examiner, on 409 observers between the ages of 11 and 18 years, of whom 371 appeared

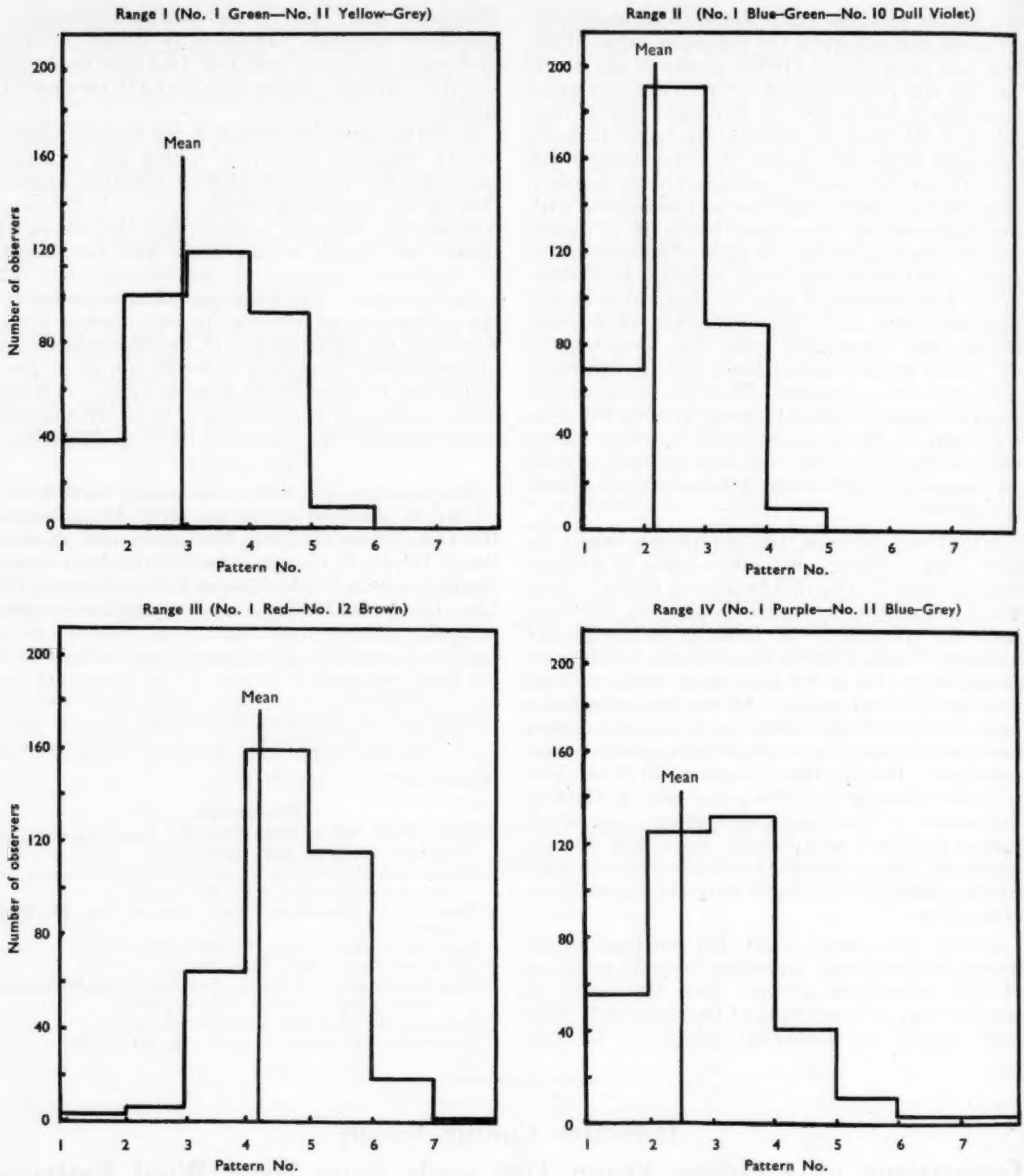

FIG. 1—Histograms of Colour Tests carried out with the Wain Test at Huddersfield College, Salford Technical High School and Huddersfield College of Technology

to have normal and 38 abnormal colour vision when subjected to the Ishihara test. The distribution of the colour-defective persons amongst five age groups is given in Table I.

TABLE I

Age	Number Tested	Number of Colour-defectives	Percentage of Colour-defectives
11–12	75	3	4
12–13	45	6	13
13–14	58	7	12
14–15	111	11	10
15–18	120	11	9

The results of the matchings are illustrated in Fig. 1 in the form of histograms, from which the average matchings were obtained.

STATISTICAL ANALYSIS OF RESULTS

The analysis of variance method was used in an attempt to diagnose defective colour vision not disclosed by the Ishihara test. The standard error of an observer's estimate was calculated, and those examinees with a deviation from mean match greater than $\pm 2\sqrt{v}$ were regarded as having doubtful colour vision. Twelve observers, normal by the Ishihara test, were found to be outside the

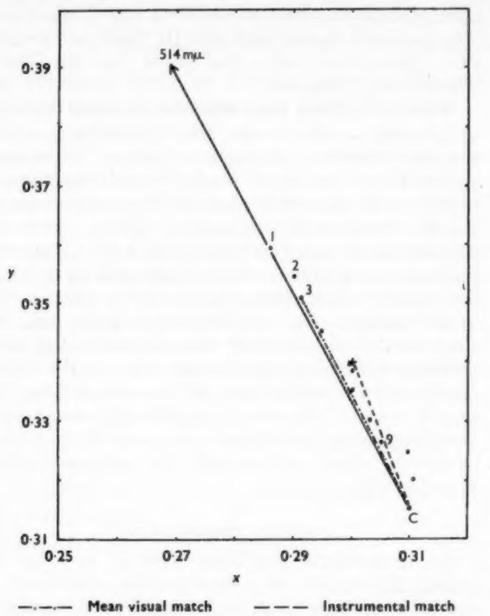

Fig. 2—Chromaticity Plots of Patterns used in Range I, showing the Dominant Wavelength of Pattern No. 1, with Standard Source C as Illuminant, and the Position of the Test Pattern +

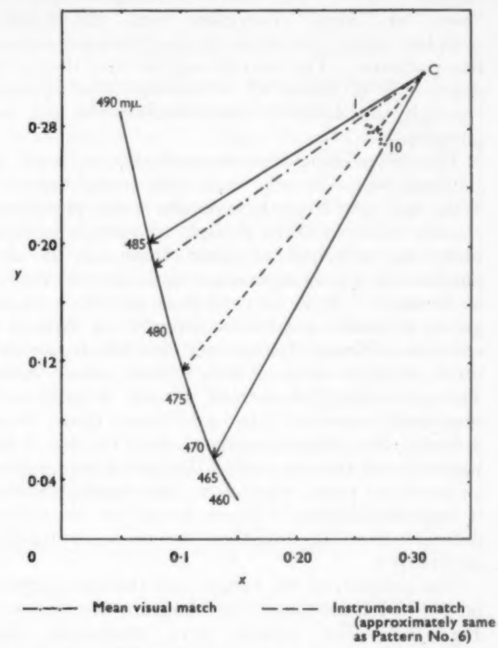

Fig. 3—Chromaticity Plots of Patterns used in Range II, showing the Dominant Wavelengths of Patterns No. 1 and 10, with Standard Source C as Illuminant, and the Position of the Test Pattern +

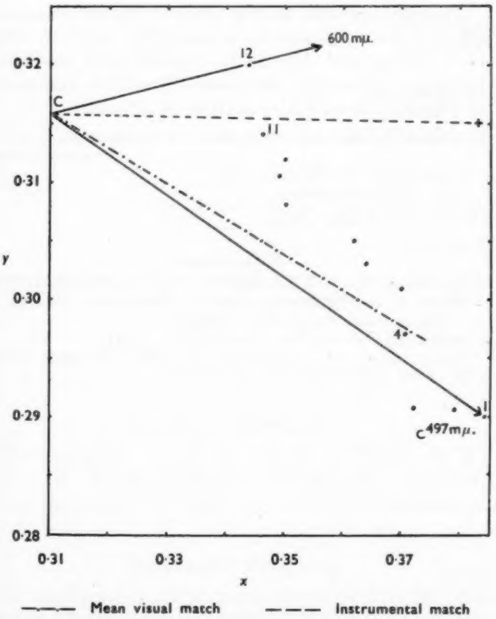

Fig. 4—Chromaticity Plots of Patterns used in Range III, showing the Dominant Wavelengths of Patterns No. 1 and 12, with Standard Source C as Illuminant, and the Position of the Test Pattern +

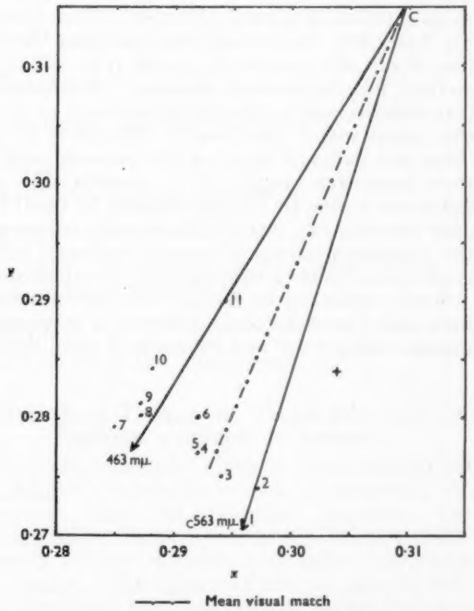

Fig. 5—Chromaticity Plots of Patterns used in Range IV, showing the Dominant Wavelength of Patterns No. 1 and 11, with Standard Source C as Illuminant, and the Position of the Test Pattern +

standard error, their matches being consistently "low" or "high", compared with the average matches, with a deviation varying between one and five patterns. The results suggest that the colour deficiency of these 12 observers was revealed through the dichroic characteristics of the test patterns.

The 38 persons who were unable to read the Ishihara test correctly were also tested with the Wain test, and from their results it was possible to classify them in three groups. Fourteen of these observers matched at least three of the test patterns in a normal manner and were referred to as Group 1. It is thought that members of this group possess a red colour-defect [2]. A further 10 examinees (Group 2) made matches which appeared quite wrong to persons with normal colour vision. The remaining 14 formed Group 3 and made abnormal matches; in addition, they found difficulty in obtaining a match with the No. 1 test pattern, and they described the hue of this pattern as brown or fawn, whereas to the normal observer it appeared green. Those found to be colour-defective from the statistical analysis were classified as Group 4.

The position of the ranges and the test patterns on the C.I.E. chromaticity diagram are shown in Fig. 2–5. The points were computed from reflectance curves measured with a General Electric recording spectrophotometer, using the "30 selected ordinate" method for Illuminant C.

EFFECT OF FIELD SIZE

From examination of the plots of the different ranges in Fig. 2–4, it is seen that the instrumental matches of the test patterns are different from the mean matches of normal observers. Test Pattern No. 4 (see Fig. 5) deviated from the other three in that it was not possible to match it to the range on the C.I.E. chromaticity diagram. Furthermore, it is situated near to the end of the range at which the visual match was made. The plots of the other test-patterns occur at the opposite ends of their respective ranges. It is possible that this difference is due to the discrepancy in the C.I.E. data (between the standard luminosity curves and the luminosity curves of normal observers) which is known to exist in this region of the spectrum [3].

Work carried out by Nasser [4], in which observers were asked to make some dichroic (or metameric) matches using 2°, 5° and 10° fields of view, showed that matches predicted by the chromaticity plots agreed with matches made with the 2° field size. The matches made with the 10° field of view did not correspond with the plots on the C.I.E. chromaticity diagram.

When the Wain test, which subtended an angle of 10° approx. at the eye, was viewed by a colour-normal observer through a yellow or orange-yellow filter, the match tended to correspond more closely with that predicted by the position on the C.I.E. chromaticity diagram. Also, when the patterns were matched in tungsten light by a person having normal colour vision, there was again closer agreement with the chromaticity plots. This would suggest that the tungsten lamp, and the filter used in conjunction with the matching lamp, reduced the short-wavelength end of the visible spectrum in a similar way to the *macula lutea*. If this is correct, the short-wavelength receptors of the retina must extend at least up to the boundary of the 10° field and outside the influence of the macular pigmentation.

COLOUR THRESHOLDS

An instrument was assembled to measure the colour thresholds of colour-normal observers, in order to compare them with some of the thresholds of the colour-defective subjects in the groups mentioned earlier. It has been found that members of Group 4, diagnosed by the results of the statistical analysis, possess colour thresholds which differ from the normal measurements in 400–450 mμ. and 600–650 mμ. regions of the spectrum. This work will be reported later.

* * *

Thanks are due to the Wool Textile Research Council for a research scholarship, and to Miss D. C. Clegg and Mr. S. L. Anderson of the Wool Industries Research Association for their assistance in connection with the statistical analysis.

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(*Received 11th May 1959*)

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[1] Jordinson, F., and Minshall, T., J.S.D.C., **75**, 585 (1959).
[2] Wain, J. G., *Fellowship Thesis* (Manchester College of Science and Technology, 1957).
[3] *Science of Colour* (New York 1953), p. 241.
[4] Nasser, M. I., *Ph.D. Thesis* (University of London, 1954).

CORRESPONDENCE

The Publications Committee does not hold itself responsible for opinions expressed by correspondents

The Physical State of Direct Dyes in Viscose Rayon and its Influence on Light Fastness

In connection with the recent letter by Weissbein [1], equally interesting results might be obtained by extending the work on light fastness to cover direct dyes of varying fastness to washing.

During my thirty years at Droylsden, millions of pounds of viscose rayon were dyed fast to washing in lingerie shades by using direct dyes such as Oxyphenine, Chlorazol Fast Orange AG and Chlorantine Fast Blues. The shades were dyed somewhat heavier than the depth ordered, and then reduced to the required depth by boiling with soap solution. No complaint of lack of fastness was ever received.

C. M. WHITTAKER

RED LEA HOTEL
SCARBOROUGH
21st December 1959

[1] Weissbein, L., J.S.D.C., **75**, 537 (1959).

The Prosperity of British Dyestuff Manufacturers before 1915

In his review [1] of J. J. Beer's book *The Emergence of the German Dye Industry*, Mr. Brightman comments that the author "notes Ivan Levinstein's familiarity with German methods in the comparative success of that British firm".

In 1915 Levinstein Ltd. paid off many years' arrears of their preference share dividends. Read Holliday & Sons Ltd. had always paid their preference dividends, whilst on their ordinary shares they paid a 5% dividend from 1906 to 1909, and 10% during 1910–1915. If Levinsteins, with these financial results, were a comparative success, what rating would be put on the success of Read Hollidays? The Government provided the answer in taking over Read Hollidays, and not Levinsteins, as British Dyes Ltd.

C. M. WHITTAKER

[1] Brightman, R., J.S.D.C., **75**, 538 (1959).

ERRATA

On p. 54 of the present volume (Jan. 1960) the first word of the title of the fifth abstract in the first column should read **Moisture** not Mixture, and on p. 123 (Feb. 1960) the second word in the title of the last abstract in the first column should read **Rhodanine** not Rhodamine.

Notes

Election of Fellows

At the meeting of Council held on 3rd February 1960 the following elections were made—

Raymond Smith Asquith
Bradford, Yorkshire; Senior Lecturer, Bradford Institute of Technology

Harold Davis Bower
George Green, near Slough, Bucks.; Senior Inspector (Textiles), Inspectorate of Stores and Clothing, War Department, Central Ordnance Depot, Didcot, Berks.

John Francis Morrison
Prestwich, Manchester; Managing Director, I. Bury Ltd., Manchester

Death of Members

We regret to report the death of Messrs. O. W. Clark, W. A. Falconer, M. Fletcher, W. Graham, J. R. Hannay, D. P. Ketner, and E. Thornton.

Polymeric Progress

A Conference on Polymeric Progress is to be held by the Plastics Institute in the William Beveridge Hall, University of London, on 30th and 31st March 1960. Fuller information is obtainable from the Secretary, The Plastics Institute, 6 Mandeville Place, London, W.1.

Huddersfield College of Technology Library Facilities available to Industry

The College Library, which now holds a complete set of British Standards, is open to commercial and industrial firms for reference purposes. The Library has a stock of over 22,000 books and 240 journals, a list of the periodicals taken is available on request. The Librarian will be glad to help inquirers in any way that lies in his power including securing loans from the National Central Library and other sources. The Library is a member of the recently established Huddersfield and District Information Scheme.

Royal Society of Arts
Sir William Jackson Pope Memorial Lecture 1960

The above lecture was delivered by Mr. Clifford Paine, an Honorary Member and the Immediate Past President of the Society of Dyers and Colourists, on 3rd February 1960, his subject being *Modern Dyes*.

Quarpel Water Repellent Finish

Work at the U.S. Quartermaster & Engineering Center, Natick, Mass., has resulted in production of a water repellent finish that resists simulated one-inch-per-hour rainfall for several days without water penetration, is oil resistant and can be laundered or dry cleaned throughout the life of the garment and still remain oil and water resistant. It consists in impregnating the cloth with a mixture of stearamidopyridinium chloride and Scotchgard FC-154 (Minnesota Mining & Mfg. Co.) (a non-ionic emulsion of a perfluoroacrylic ester), drying and curing. The two components are synergistic as neither alone withstands repeated washing or dry cleaning. The process is available for general use without any need for a licence to be obtained.

Textile Institute
New Chairman of Council and Honorary Secretary

Dr. A. R. Urquhart, a member of the Society, who has been Honorary Secretary of the Textile Institute since 1958 is leaving that office to become Chairman of the Council of the Institute, the former Chairman, Mr. G. Loasby, also a member of the Society, finding it necessary to resign because of business engagements abroad. The new Honorary Secretary of the Institute is Mr. J. C. H. Hurd, Head of the School of Textiles of Leicester College of Technology and Commerce.

Paint Research Association

Dr. L. Valentine, a former Lecturer in the Chemistry of High Polymers at Leeds University, has been appointed by the Council of the Research Association of British Paint, Colour and Varnish Manufacturers as Director of Research at the Paint Research Station, Teddington. He will take up his new duties on 1st April 1960.

The Rôle of Management in an Industrial Society

A conference to discuss the above subject is being held on 31st March and 1st April 1960 at Leamington Spa by the British Institute of Management. Details are available from the General Secretary, British Institute of Management, 80 Fetter Lane, London, E.C.4.

Residential Courses of Study in Management Practice

The British Institute of Management has organised two residential courses of study in Management Practice to be held in Wadham College, Oxford, on 2nd–9th April and 23rd–30th July 1960. Full details and forms of application are available from the General Secretary of the Institute whose address is given in the preceding note.

World Congress for Man-made Fibres London 1962

The 2nd World Congress for Man-made Fibres will be held in London from Tuesday 15th to Friday 18th May 1962. (The 1st World Congress was held in Paris in 1954 and was attended by delegates from 33 countries.)

Inquiries regarding the Congress should be addressed to Dr. L. Landsman, International Rayon and Synthetic Fibres Committee, 29–31 Rue de Courcelles, Paris 8, France.

Mechanical Handling Exhibition London 3–13 May 1960

This exhibition, claimed to be the world's largest exhibition of labour-saving equipment, will occupy over 500,000 sq.ft. at Earls Court. Full information, programme of film sessions, details of travel and hotel facilities and free admission tickets can be obtained from Mechanical Handling, Dorset House, Stamford Street, London, S.E.1.

Meetings of Council and Committees February 1960

Council— 3rd
Finance and General Purposes— 3rd
International Federation 1959 Congress
  Planning and Co-ordinating— 12th
Publications— 16th
Colour Index Editorial Board— 16th

Meeting of I.F.A.T.C.C. Council

Council of Delegates— 26th

OBITUARY NOTICE

Wilfred Kershaw, O.B.E, F.T.I, F.S.D.C.

Wilfred Kershaw, who died in August last, was born in 1879. His first post in industry was in a cotton bleach works which he left to enter the teaching profession. During the First World War he was engaged in the production of pure cotton cellulose needed for making cordite. After the war he joined the staff of the Bleachers' Association Ltd., of which he later became a director. It was here that he became one of those responsible for the development and introduction to the textile trade of the now universally used viscosity test. He was a member of the Society for a great many years up to his death, being a regular attender at the meetings of the Manchester Section.

New Books and Publications

Die Physik der Hochpolymeren
Vierter Band
Theorie und Molekulare Deutung Technologischer Eigenschaften von Hochpolymeren Werkstoffen

Edited by H. A. Stuart. Berlin: Springer Verlag. 1956. Pp. xx + 667. Price, DM 89.00.

The popularity of books containing a collection of specialist articles by different authors is increasing. Whilst this type of publication has much to commend it, the reader often finds that only specific parts are of value to him, whilst other parts are so highly specialised as to be unintelligible. Much depends on the careful selection by the editor of suitable authors. In the present volume this has been done with considerable care, and the book covers the scope of its title extremely well.

The elastic and non-elastic properties of polymers in solid and solution are ably dealt with. Other chapters cover structure in relation to mechanical properties in the separate cases of rubbers, fibres and plastics. There is a most interesting chapter on the relationship of structure to electrical properties. The reviews are not confined to synthetic material and it is refreshing to see that, at least in physical properties, such as creep relaxation effects, the similarities between natural and synthetic materials are well described. Each chapter gives ample, but not excessive, references to the original work.

Some readers may find that the continual changes from German to English, with different authors, is a nuisance, and the volume is definitely not light reading. The printing is of a high standard and the editor is to be commended on the care taken to avoid small errors of type.

It is, however, the type of book most research workers will expect to find on library shelves rather than in their own private collection.

R. S. Asquith

Technique of Organic Chemistry
Volume 1
Physical Methods of Organic Chemistry
Part I

Edited by A. Weissberger. Third completely revised and augmented edition. Pp. xii + 894 + I1–I24. New York and London: Interscience Publishers. 1959. Price. 184s. 0d.

This work has been extended from three parts of 2500 pages to four parts of more than 3500 pages containing sixteen new chapters on recently developed methods or on topics now needing more extensive treatment than was given in the second edition. This third edition of Part I actually contains one chapter less than that of the second edition. Comparison with the chapter headings given when this part was reviewed on its previous appearance (J.S.D.C., **67** (1951) 118) reveals how completely it has been rewritten, the chapters now being—

I— *Automatic Control.* J. M. Sturtevant
II— *Automatic Recording.* D. R. Simonsen
III— *Weighing.* A. S. Corwin
IV— *Determination of Density.* N. Bauer and S. Z. Lewin
V— *Determination of Particle Size and Molecular Weight.* G. L. Beyer
VI— *Temperature Measurement.* J. M. Sturtevant
VII— *Determination of Melting and Freezing Temperature.* E. L. Skau, J. C. Arthur, Jr., and H. Wakeham
VIII— *Determination of Boiling and Condensation Temperatures.* W. Swietoslawski and J. R. Anderson
IX— *Determination of Vapour Pressure.* G. W. Thomson
X— *Colorimetry.* J. M. Sturtevant
XI— *Determination of Solubility.* W. J. Mader, R. D. Vold, and M. J. Vold
XII— *Determination of Viscosity.* J. F. Swindells, R. Ullman, and H. Mark
XIII— *Determination of Properties of Insoluble Monolayers at Mobile Interfaces.* A. E. Alexander
XIV— *Determination of Surface and Interfacial Tension.* By the late W. D. Harkins. Revised by A. E. Alexander.
XV— *Determination of Osmotic Pressure.* R. H. Wagner and L. D. Moore, Jr.

There is a 24 pp. subject index.

Its contents make it a necessary work of reference to all workers interested in the subjects discussed. As an example of book production it could scarcely be bettered.

C. O. Clark

Advances in Spectroscopy
Volume 1

Edited by H. W. Thompson. Pp. ix + 363 + 21 half-tones. New York and London: Interscience Publishers. 1959. Price, 85s. 0d. ($12.50).

The first in a series of annual volumes which will present, interpret and evaluate significant recent accomplishments in spectroscopy. Applications and techniques that will be dealt with will vary from fundamental research to routine analysis. The contents of this volume are—

Spectra of Polyatomic Free Radicals. 185 references. Pp. 1–55. D. A. Ramsey
Spectroscopy in the Vacuum Ultraviolet. 72 references. Pp. 56–75. W. C. Price
Index of Refraction of Air. Pp. 76–8. D. H. Rank
Determination of the Velocity of Light. Pp. 79–90. D H. Rank
High Resolution Raman Spectroscopy. 135 references. Pp. 91–174. B. P. Stoicheff
Modern Infrared Detectors. 87 references. Pp. 175–213. T. S. Moss
Infrared Spectra of Polymers. 111 references + list of several hundred papers. Pp. 214–287. A. Elliott

Rotational Isomerism about C–C Bonds in Saturated Molecules as Studied by Vibrational Spectroscopy. 212 references. Pp. 288–353. N. Sheppard.

C. O. Clark

Physical Methods of Investigating Textiles

Edited by R. Meredith and J. W. S. Hearle. Pp. ix + 411 + 13 half-tone inserts. New York and London: Textile Book Publishers Inc. A Division of Interscience Publishers Inc. 1959. Price, $13.00 or 88s. 0d.

This book has grown out of a course of lectures held in the Manchester College of Science and Technology in the winter of 1956–7. The stated aim is to describe experimental methods of determining the structure and physical properties of textiles, with the emphasis on newer techniques.

The chapters are headed X-Ray techniques, Infrared spectroscopy, Electron microscopy, Optical microscopy, Fibre dimensions, Density, moisture and swelling, Yarn and fabric structure, Mechanical properties of fibres and yarns, Some mechanical properties of fabrics, Transmission of heat, moisture and air, Frictional behaviour of textiles, Optical properties, Electrical properties, Applications of nuclear physics. There are twelve authors, including the two editors.

The book is well produced with clear diagrams and intelligent legends, an excellent index and ample cross-references.

When one book covers such a wide range of topics contributed by several authors it is inevitable that there will be some variation between chapters in interest and originality according to the reader's interests and the quality of previous publications; moreover, the individual reader will always find some unnecessary paragraphs or regret some omissions. This book is no exception, but to criticise the contents would be to quibble, for capable authorship, careful editing and a wealth of literature references have resulted in a book which is readable throughout and will be generally acceptable as an informative (and decorative) addition to the library of undergraduate and post-graduate. The library would be enhanced if this book is accompanied by Wood's *Physics of Fibres*, Kaswell's *Textile Fibres, Yarns and Fabrics* and appropriate sections of *Review of Textile Progress*.

W. Guy

Measuring and Predicting the Generation of Static Electricity in Military Clothing

A. M. Crugnola and H. M. Robinson. *Textile Series Report No. 110.* Pp. vi + 64. Natick, Massachusetts: Quartermaster Research and Engineering Center, Textile, Clothing and Footwear Division. 1959. n.p.

The obvious dangers of static discharges when handling fuels or explosives have prompted this detailed investigation of the problem. The report is divided into five sections which cover in turn the theory of charge and discharge, field data, the evaluation of antistats, a static meter designed during the investigation and the effect of other finishes on antistatic agents.

The report is military in style, naturally. It is a little longer than Caesar's alliterative despatch and uses words less simple than those employed by a more recent commander associated with the letter V. But it is relatively short and pertinent. This in itself is sufficient recommendation to those interested in the problem; but in addition there is a good deal of new thinking included which is of considerable importance to all textile processors, particularly those handling fully-synthetic fibres. The proprietary antistats examined are all of the wash-fast class but unfortunately— perhaps with understandable reticence— only relatively vague indications are given of the chemical classes into which they fall. The review of other instruments used for measuring the static propensity of textiles shows the difficulty of relating inter-laboratory results and the need for standardisation. The Quartermaster device could well become the norm.

S. R. Cockett

Aspects Scientifiques de l'Industrie Lainière

By F. Monfort. Pp. xviii + 514. Paris: Dunod. 1960. Price, 7,000 francs.

This book, by the Secretary of the Technical Committee of the International Wool Federation, surveys recent researches and developments in the wool processing industries and particularly from the viewpoint of the application of statistical methods. Though primarily written for the spinner and weaver, its clarity of exposition and the general manner in which the subjects discussed are treated renders it suitable for use by those engaged in other branches of the industry.

C. O. Clark

Drycleaning Technology and Theory

A Report of the National Institute of Drycleaning

By A. R. Martin and G. P. Fulton. 1958. Pp. viii + 269. New York: Textile Book Publishers Inc. A Division of Interscience Publishers Inc. Price, $6.00 (40s. 0d.).

This well-written volume, by two members of the staff of the National Institute of Dry Cleaning, U.S.A., is the first real attempt to survey the existing knowledge of the scientific processes involved in dry cleaning. There is therefore little attempt to deal with any of the technological aspects of dry cleaning. The literature concerned with natural and artificial soils, the application of artificial soiling and the use of artificially soiled textiles for determining detergency are well drawn together and should serve as a useful guide to a new worker in this field, preventing well-known pit-falls. The survey of knowledge and literature for the detergent process in aqueous systems is incomplete by intent and only covers those factors which have an analogy with factors involved in the more complex study of non-aqueous detergency.

The subject is expanded into a consideration of the theory and control of charge system methods in dry cleaning processes wherein dry cleaning soaps and water are solubilised in the solvent. Finally some insight is given into the scientific principles underlying garment finishing.

The text is supported by 250 references to the literature, a small percentage of which is inaccessible.

Readers outside the U.S.A. should be advised that the section dealing with dry cleaning solvents applies particularly to the U.S.A. and this applies especially to Stoddard Solvent instead of which White Spirit is used in the U.K. The relative usage of petroleum hydrocarbons and chlorinated hydrocarbons as cleaning solvents varies from country to country for technical and commercial reasons.

E. J. Davies

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

J. R. Geigy A.G.

Reactone Dyes in Printing— This card contains prints on cotton cloth of ten Reactone dyes, a new range of reactive dyes for printing cellulosic fibres. They are applied in pastes containing alginates as thickeners, sodium carbonate to promote combination of dye and fibre and urea to increase solubility and colour yield. These dyes have virtually no affinity for cellulose and there is thus no migration of unfixed dye on to adjacent parts of the material. After printing the material must be thoroughly dried but need not be fixed immediately; protection from moisture and acid vapours must be given. Fixation can be in neutral steam for 7–10 min. or by dry heat for 4–6 min. at 150°c. As is to be expected, complete removal of uncombined dye is essential for development of maximum wet fastness and this is achieved by thorough washing in cold water followed by soaping at the boil; this is particularly important with the Turquoise Blue FGL. Reactone dyes can be applied on naphthol prepares and alongside vats, solubilised vats, resin-bonded pigments and Iragen and Iratral dyes. The colour range includes yellow, orange, red, violet, blue, navy, grey, and black. The lowest light fastness in standard depth is 5, with two ratings 6–7, another 7, and one (black) 7–8; minimum washing fastness (ECE Test C) is 4–5; 5 in eight cases.

L. B. Holliday & Co. Ltd.

Elbelan Colours— This card contains dyeings in six depths on wool slubbing of the first six of a range of 2:1 dye:metal complex dyes. They are recommended to be applied from ammonium sulphate or acetic acid dyebaths at pH 6 or slightly lower, under which conditions it is claimed that risk of damage to the fibre is reduced to a minimum. They are of excellent fastness to light, even in pale dyeings, and good fastness to wet treatments and are completely compatible with each other in dyeing behaviour. They are also of interest for dyeing nylon, addition of Leveller WA New being advised in this case. The fastness to light of standard depth dyeings is 6–7 or better, to washing 5, and to alkaline milling 5 in all cases.

Estersol Golden Yellow IRK— This solubilised vat dye gives bright reddish yellows on cellulosic fibres. It has good affinity in presence of electrolyte and can be applied on the jig or winch as well as by padding. It is also suitable for direct printing and for white resists using Erasol C, Eratrope W and sodium acetate. Fastness figures on cotton include— Light (daylight) 6–7, washing (S.D.C. Test 2) 5, chlorine 4–5.

Estersol Green IB— This solubilised vat dye gives bright bluish greens on cellulosic fibres. It has good affinity and may be applied in circulating-liquor machines, on the winch and on the jig, as well as by padding. It is also of interest in printing for both direct and resist styles. It is also recommended for use on wool for which it has high affinity and to which it is applied from a weakly acid dyebath followed by development with acid dichromate. Fastness figures on cotton include— Light (daylight) 6–7, washing (S.D.C. Test No. 2) 5, chlorine 4, weathering 7.

Monochrome Brown EB— This chrome dye gives full browns of excellent fastness to light and wet treatments on wool. It yields dyeings of the highest fastness when dyed afterchrome but may also be applied by the single-bath and on-chrome methods. It is particularly recommended for dyeing loose wool and slubbing and is also of interest for Vigoureux printing. Fastness figures for an afterchrome dyeing on wool include— Light 4–5, milling 4–5, potting 3–4.

Monochrome Brown B— This standard chrome brown which has long been available in paste form is now marketed as a powder. Low solubility in cold water necessitates dyeing being started at not less than 60°c. Fastness figures for a single-bath chrome dyeing on wool include— Light 5, alkaline milling 4–5, potting 3.

Monochrome Brown KE— This chrome dye is recommended for use, alone and in mixtures, on wool at all stages of processing, particularly where high fastness to light and carbonising is demanded of pale dyeings. It is also of interest for afterchrome dyeing silk and nylon. Fastness figures on wool include— Light 6, milling 5, carbonising 5.

Monochrome Orange R— This chrome dye is particularly recommended for economical browns, drabs, and khakis on all forms of wool, maximum fastness being obtained by dyeing afterchrome or single-bath chrome. It is also of interest for direct printing on cloth and mélanging, and for dyeing nylon and silk. Fastness figures for an afterchrome dyeing on wool include— Light 4–5, alkaline milling 4, washing 5.

Erasol K— A water-insoluble sulphoxylate formaldehyde for direct or discharge printing of vat dyes on cellulose acetate and nylon. Its low solubility greatly reduces the risk of "flushing" even under fairly damp steaming conditions. It is also of interest for stripping, tendering of the material often associated with the normal methods being reduced or even eliminated.

Paradone Yellows 4GF and 8GF— These anthraquinonoid vat dyes give bright greenish yellows on cellulosic materials and are particularly suitable for curtains and awnings since they do not cause catalytic tendering or fading. They are very suitable for printing by the potash–Erasol C process without pre-reduction and also by the Colloresine process. They are available as paste, powder fine for dyeing and as highly dispersed powder, the latter being particularly suitable for pigmentation. Fastness figures on cotton for both dyes include— Light 7, soda-boiling 4–5, chlorine 5.

Supracet Navy Blue T: Supracet Dark Blue TG— These two disperse dyes are primarily intended for dyeing polyester fibres, either > 100°c. or in presence of carriers, preferably of the salicylic acid ester type since they are alkali-sensitive and thus alkaline solutions of carriers of the o-phenylphenol type are unsuitable. The dyebath must be neutral or faintly acid (pH 5–7) and addition of 0·25 g./l. ammonium sulphate is recommended. Scouring or, in the case of heavy dyeings, reduction-clearing is essential after dyeing to develop maximum fastness. Both dyes are also of interest on Acrilan. Fastness figures for both dyes on Terylene include— Light (daylight) 6–7, washing (S.D.C. Test No. 2) 5, sublimation 5, milling 5.

Sandoz A.G.

Artisil Violet RFL: Foron Blue 3RFL— This disperse dye is of particular interest for bright reddish violets on secondary cellulose acetate, triacetate, and polyester fibres. It gives dyeings of very good fastness to light on all these fibres and of good to very good fastness to wet treatments and dry heat and steam heat on

polyesters to which it is applicable by both carrier and high temperature methods. It is also of interest for direct printing. It may be applied to polyamide fibres but does not build-up so well and the fastness of dyeings to light is lower. Fastness figures on secondary cellulose acetate include— Light (Daylight ISO) 7–8, washing (ECE 60°c.) 3.

Cuprofix Grey C–BL: Cuprofix Printing Grey C–BL— This homogeneous direct dye gives neutral greys on cellulosic fibres when aftertreated on the fibre with either copper sulphate/acetic acid, Cuprofix SL or Resofix CU. It is very soluble and stable in boiling neutral dyebaths and may be applied by H.T. methods, by pad–steam and by Pad–Roll. It covers dead cotton well. It is very suitable for direct printing and dyeings and prints are unaffected by crease-resist finishing. Fastness figures for a dyeing on cotton aftertreated with copper sulphate/acetic acid include— Light (Daylight ISO) 6–7, washing (ECE 60°c.) 5, perspiration ECE 4–5.

Foron Dyestuffs on Polyester Fibre and Polyester Fibre Blends— This card contains dyeings in six depths on Dacron cloth of 14 disperse dyes of the Foron range including a navy and a black. This range has been specially developed for dyeing polyester fibres using either carriers (Dilatin DB or TC) or H.T. (> 100°c.) methods. They are marketed as very finely divided powders (particle size 0·5–1 μ.) and are very readily dispersible and level dyeing, being suitable for application on the jigger, winch, and circulating-liquor machines. Rate of dyeing curves are provided for standard depth dyeings of each dye based on application (1) over the range 20–100°c. in presence of Dilatin DB and (2) from 90–140°c. The text gives details of both carrier and H.T. dyeing methods and also for dyeing polyester fibre/cellulosic fibre and polyester fibre/wool mixtures.

Cotton and Rayon Prints with Sandothrene and Tetra Colours. No. 1272/59— This card, which replaces No. 883, contains direct prints in two depths on cotton and spun viscose rayon cloth of all (64) the Sandothrene and Tetra vat dyes suitable for printing cellulosic fibres. They are divided into two groups. The first contains 10 dyes not approved for the Felisol fastness label and the second 54 which have been so approved and carry the additional suffix F– before the other brand letters. Fastness data include light (at three depths), washing at 100°c. with soap and soda, and chlorine.

Drimarene-Z Reactive Dyestuffs for Prints on Cellulosic Fibres— This card contains direct prints on cotton, mercerised cotton, and spun viscose rayon cloth of eleven reactive dyes forming a new range specially developed for printing cellulosic fibres. They are supplied in concentrated form only and are characterised by simplicity of application and very good stability in the printing paste itself. Alginates are recommended as thickeners but emulsion thickenings may be used. The alkali used is sodium carbonate and urea is added to increase the colour yield, this being particularly important with regenerated cellulose. Fixation is by either neutral steaming for 8–12 min. or baking for 6 min. to 45 sec. at 140°–190°c. With dry-heat fixation the urea content must be increased to at least 200 parts per 1000. Removal of unfixed dye after printing must be complete but a notable advantage claimed for these dyes is the ease with which this may be achieved. They can be printed alongside vats, solubilised vats, stabilised azoic combinations and resin-bonded pigments and are also suitable for coloured resists under aniline black and padding on white or coloured resists. Fastness ratings include— Light (daylight) (standard depth) 5 or better, with 7 for Yellow Z–3GL and Violet Z–RL and 7–8 for Black Z–BL; washing ISO (95°c.) 5 in the majority of cases and never less than 4.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., 68, 23 *(Jan. 1952) and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Europe's Model Textile Finisher (Process Control at the Royal Twentsche Steam Bleachery)
F. G. C. Meyer
Amer. Dyestuff Rep., 48 (1 June 1959) 31–6

The water supply system and continuous bleaching and dyeing ranges of the Royal Twentsche Steam Bleachery (T.S.B.) of Goor, Holland, are described with illustrations, with emphasis on process control. Water flow and purity are continuously recorded and regeneration of the demineralising plant is also controlled from the same instrument panel. The liquor levels, reagent concentrations and temperature in the continuous dyeing and bleaching ranges are automatically recorded and maintained.
W.P.M.

PATENTS

Preparing Pellets from Powdered Materials
Cawood Wharton & Co. *BP* 825,703

Apparatus Resistant to Acid Chlorite Solutions
Deutsche Gold- und Silberscheideanstalt *BP* 817,615

Aluminium coated by the eloxal process (i.e. electrolytically oxidised in an acid electrolyte) is resistant to acid chlorite and chlorine dioxide solutions in absence of nitrate or phosphate ions. C.O.C.

Drying Loose Fibres, Corded Laps, etc.
Erich Kiefer Lufttechn. Anlagen and Erich Kiefer, Konstruktions *BP* 826,785

When drying over a series of perforated drums rotating successive drums at different speeds distorts the material sufficiently to alter the relative position of the fibres and thereby ensures that the drying air acts uniformly upon all the layers of the material. C.O.C.

Reclaiming Dry-cleaning Solvent
Vic Manufacturing Co. and Butler Manufacturing Co. *USP* 2,893,925

Silicon Dioxide (C.I. 77811) (IV p. 197)
Pad–Roll Dyeing (VIII p. 202)

II—WATER AND EFFLUENTS

PATENT

Coagulating Aqueous Dispersions
National Aluminate Corpn. *BP* 826,770

Addition of 0·1 p.p.m. of a hydrophilic alkylene polyamine polyfunctional halogeno polymer solution (obtained by condensation–polymerisation of an alkylenepolyamine and a polyfunctional halogenohydrin in aqueous solution to a thickened condition short of gel formation) is an effective coagulant for fine dispersion of predominantly inorganic compounds, e.g. the suspension obtained in the lime–soda water softening process.
C.O.C.

Testing Solids, Liquids or Gases for Presence of Substances forming Azo Dyes (XIV p. 204)

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Miscibility of Organic Solvent Pairs
W. M. Jackson and J. S. Drury
Ind. Eng. Chem., 51 (Dec 1959) 1491–3

Tables giving the degree of miscibility of each of 72 solvents with each of the others. C.O.C.

Some Recent Advances in the Chemistry and Biochemistry of Commercially Important Condensed Tannins
D. G. Roux *J. Amer. Leather Chem. Assocn.*, 54 (Nov 1959) 614–627

The tannins of wattle and quebracho extract consist of a mixture of components representing an even mol. wt. gradation over the ranges 550–3250 and 800–2350 respectively. From black wattle extract (−)-7,3′,4′,5′-tetrahydroxyflavan-3-ol ((−)-robinetinidol), first of the resorcinol series of naturally occurring catechins, (+)-catechin and (+)-gallocatechin have been identified, and their distribution in related wattles established. The

detailed chemistry of (−)-7,3′,4′-trihydroxyflavan-3,4-diol ((−)-leucofisetinidin), shown to be a prototype of quebracho tannins, is described. Support for the concept of flavan-3,4-diols (I) as basic units of condensed tannins is obtained also from mangrove bark extract and other sources, and possible mode of linkage of I to other or similar "flavonoid" nuclei in tannin formation is discussed. The importance of these advances to some aspects of leather chemistry, e.g. redness of vegetable extracts, their reaction with bisulphite, identification of condensed tannins in leather, and the tannin–collagen affinity relationship, is reviewed. H.H.H.

PATENTS

Surface-active Substances
Henkel & Cie. *BP* 826,171

Products especially suitable as dispersing agents and additives to other emulsifying agents are obtained by reacting 2 mol. of a diisocyanate with 1 mol. of a dialkylolamide and heating the product with a polyglycol ether. C.O.C.

Mixed Non-ionic–Anionic Emulsifiers
Atlas Powder Co. *BP* 819,035

An alkylarylsulphonic acid (Alk of 8–18 C) or a sulphated hydroxy compound containing at least one hydrocarbon chain of 8–18 C is neutralised with an inorganic base in presence of a non-ionic partial fatty acid ester (acid of $>$ 11 C) of a polyhydric alcohol or a polyoxyethylene ether of a compound containing a hydrophobic hydrocarbon radical. The product is an emulsifier for forming oil in water emulsions. C.O.C.

Surface-active Polyester Detergents
Henkel & Cie. *BP* 818,334

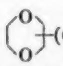
The polyglycol esters of dicarboxylic acids containing a lipophilic residue of 15–50 C and at least one carbonamide group have excellent detergent properties. C.O.C.

Detergent having Good Foaming Power at High Dilution
Dutton & Reinisch *BP* 818,158

A mixture of an anionic detergent, a fatty acyl-alkylolamide and a non-ionic detergent containing a polymerised ethylene oxide chain has good foaming power at high dilution. C.O.C.

Antistatic Agent and Plasticiser
Chemische Werke Hüls *BP* 826,798

Ethers of formula—

 $(OR)_x$

(R = a monovalent saturated or unsaturated aliphatic radical of one H, 2–20 C and one or more O atoms in ether linkage; x = 1–4) e.g. di-[β-(β'-ethoxy)-ethoxy-ethoxy]-dioxane, have excellent antistatic action and are true plasticisers. Incorporated in high molecular compounds they are not dissolved out by water. C.O.C.

Wetting and Dispersing Agents containing a Water-soluble Lignosulphonate
Monsanto Chemical Co. *USP* 2,893,913

A mixture of a lignosulphonate (10–35%), a rosin acid–ethylene oxide condensate (30–80) and an acetylenic glycol (10–35) of formula—

$$R^1R^2{\cdot}HOC{\cdot}C{:}C{\cdot}COH{\cdot}R^3R^4$$

(R^1, R^2, R^3, and R^4 = Alk of $<$ 7 C) e.g. 2,4,7,9-tetramethyl-5-decyne-4,7-diol is a wetting and dispersing agent which can be used in either soft or hard water. C.O.C.

Water-repellent Finish
Deering Milliken Research Corpn. *BP* 823,168

Modification of *BP* 804,509 (J.S.D.C., **75** (1959) 133). Improved results are obtained by incorporating in the emulsion a compound supplying alkaline earth metal and/or magnesium ions. C.O.C.

Dispersions of Hydrocarbon Resins
Esso Research & Engineering Co. *BP* 818,735

Aqueous dispersions of high shelf and mechanical stability are obtained by mixing the resin and water, between the resin m.p. and 100°C., with a mixture of a compound of formula—

$$R^1(OCHR^2CHR^2)_nOH$$

(R^1 = Alk or aralkyl; R^2 = H or Alk; n = 4–10) and one of formula—

$$R^3N\begin{cases}(CH_2CH_2O)_xH\\(CH_2CH_2O)_yH\end{cases}$$

(R^3 = aliphatic hydrocarbon of 10–20 C; $x + y$ = 2–10) and adding water until an inversion of phase occurs. The products are impregnating and coating agents for cloth or paper. C.O.C.

Bonding Agents for making Bonded Fibre Fabrics
R. J. Spahr, J. K. Sumner, and E. J. Yedlick *BP* 818,416

Use of copolymers of vinyl acetate and aralkyl acrylate and/or methacrylate containing $\not<$ 70% vinyl acetate, yields strong and soft fabrics having high wet strength and wet abrasion resistance. C.O.C.

Reactive Fluorocarbon Compounds useful as Surfactants and Intermediates
Minnesota Mining & Manufacturing Co. *BP* 818,756

Compounds of formula—

$$C_nF_{2n+1}SO_2NHCH_2CH{:}CH_2$$

(n = 3–12), particularly *N*-allyl perfluorooctane sulphonamide $C_8F_{17}SO_2NHCH_2CH{:}CH_2$, have unique surface-active properties because of their fluorocarbon group which is both hydro- and oleophobic. They become increasingly insoluble in water with increase in length of this group. The allyl group renders them more insoluble in water but makes them soluble in hydrocarbon and oils. Thus one end of the molecule is oleophobic while the other is oleophilic and both are hydrophobic. C.O.C.

Rosin Compositions stabilised against Crystallisation
American Cyanamid Co. *BP* 817,741

Addition of a condensate of a rosin and a saligenin which is soluble in molten rosin stabilises rosins against crystallisation. C.O.C.

Stabilised Aqueous Colloidal Solutions of Silica
Atlantic Refining Co. *BP* 826,219

Aqueous colloidal solutions of silica are stabilised by adding $\not<$ 1·5% (on weight of SiO_2) of ammonia, keeping the ammonia in the solution for 1–16 hr. and then removing the ammonia. The increase in stability is proportional to the time of treatment, maximum stability being obtained in 16 hr. C.O.C.

Metal Soap Driers
"Shell" Research *BP* 825,805

Mixtures of drying metal soaps of petroleum naphthenic acids and Koch acids have greater metal to organic residue ratio than conventional naphthenates as well as lower viscosity and better colour. Koch acids are obtained by treating olefins of $>$ 3 C with CO or HCOOH in absence of added water and presence of a concentrated acid as catalyst and then treating the reaction mixture with water. C.O.C.

Tanning Extracts
Svit *BP* 818,034

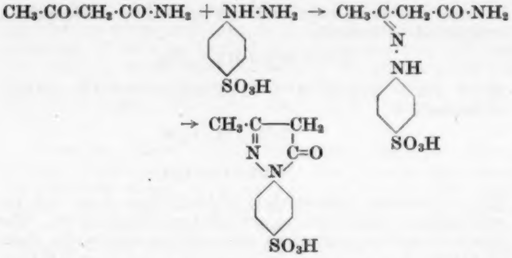
Raw vegetable tanning materials are extracted with an aqueous solution of an alkaline metal or ammonium carbonate, hydroxide and/or sulphite at pH $>$ 5. The extract is then treated with a cation exchanger to remove cations. This enables higher yields of extract to be obtained particularly in the case of tanning materials of a condensed catechol nature. C.O.C.

Polymers as related to Fabric Processing (X p. 203)
Copper Formate as a Rotproofer for Cotton (X p. 204)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

1-(4′-Phenylsulphonic Acid)-3-Methyl-5-pyrazolone from Acetoacetamide
P. A. Levin *Zhur. priklad. khim.*, 32 (Oct 1959) 2361–3

1-(4′-Phenylsulphonic acid)-3-methyl-5-pyrazolone can be prepared in bulk by treating phenylhydrazine-*p*-sulphonic acid with acetoacetamide.



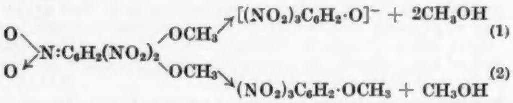
The acetoacetamide is made by dissolving diketene in 6% NH_4OH at 7°C. and is added to the aq. suspension of hydrazine. Acetoacetamidephenylhydrazone sulphonic acid is converted to the pyrazolone by acidification with H_2SO_4 or HCl. Ring closure is completed by stirring at 45°C. for 40 min., and the pyrazolone filtered off at 8°C. A 99·7% yield is obtained with HCl and 89·6% with H_2SO_4. The pyrazolone is a white powder, which behaves as a dibasic acid. T.Z.W.

Coloured Alkali Salts from *sym.*-Trinitrobenzene Derivatives
R. C. Farmer

I—Picryl Derivatives

J.C.S. (Nov 1959) 3425–3430

In water, the coloured salts undergo two types of decomp.—



of which (1) is gradual and (2) very rapid and via the nitronic acid. Picric acid forms the cpd. with methanolic alkali with difficulty, but under certain conditions unstable red soln. may be obtained. The primary product of the action of a methoxide on picryl chloride, containing Cl and OCH_3, acts in a dual capacity and leads to further reactions following two different routes, one very rapid and the other very slow; each leads to the same final product methyl picrate.

II—Phenoxy-compounds

Ibid., 3430–3433

These cpd. are analogous to the alkoxy-deriv., but are very unstable, being readily dissociated to the free nitronic acids, which decomp. immediately to the initial trinitro-cpd. The phenoxy-groups are readily irreversibly displaced by OCH_3 in presence of methoxide.

III—Picramide Derivatives

Ibid., 3433–3436

Picramide and its *N*-methyl and *N*-phenyl deriv. react with methoxide in the same manner as trinitrobenzene. The coloured amino-cpd. differ from the corresponding phenoxy-cpd., losing their OCH_3 groups on acidification, the amino- or anilino-group remaining attached to the benzene ring. Trinitrophenylmethylnitramine splits off its nitroamino-group gradually and this is accompanied by a secondary reaction in which a nitro-group in the benzene ring is replaced by OCH_3, forming two isomeric cpd., 2-methoxy-4,6- and 4-methoxy-2,6-dinitro-phenylmethylnitramine. H.H.H.

Influence of the Space Factors on the Properties of Dyes containing a Diphenyl Nucleus. XII—Disazo Dyes from *p*-Aminobenzoyl Derivatives of 4,4″-Diamino-*p*-terphenyl
H. N. Titarenko and B. M. Krasovitskii

Ukrain. khim. zhur., **25** (May 1959) 617–9

Disazo dyes from mono- and di-*p*-aminobenzoyl derivatives of 4,4″-diamino-*p*-terphenyl were prepared and compared with the corresponding dyes from *p*-phenylendiamine and benzidine. They showed increased affinity for cotton. With dyes from monoaminobenzoyl derivatives increase in the number of benzene nuclei in the molecule caused increase in depth of colour. This was not observed with dyes derived from diaminobenzoyl compounds. L.S.L.

The Separation Component in the Synthesis of Organic Dyes. IV—Modification of the Blue Component in the Synthesis of some Asymmetric Azo Dyes
I. Reichel, A. Demian, and E. Secosan

Acad. rep. populare Romîne, Baza cercetări ştiinţ. Timişoara, Studii cercetări ştiinţ., Ser. ştiinţe chim. **4** (1957) 35–46

Chem. Abs., **53** (10 Oct 1959) 18489

Asymmetric azo dyes were prepared by coupling e.g. tetrazotised benzidine or 2,2′-diaminodiphenyl with 1 mol. of salicylic acid and with 1 mol. of H acid or its *N*-acetyl or 2-phenylazo, etc. derivatives, and also by coupling diazotised *m*-(and *p*-)nitroaniline with salicylic acid, reducing the NO_2 group, diazotising, and coupling with the same H acid derivatives. The colours of the dyes are recorded. E.S.

Azo Dyes from Substituted 2-Aminothiazoles
J. B. Dickey, E. B. Towne, M. S. Bloom, W. H. Moore, H. M. Hill, H. Heynemann, D. G. Hefberg, D. C. Sievers, and M. V. Otis

J. Org. Chem., **24** (1959) 187–196

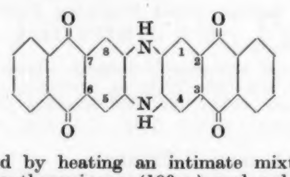
Chem. Abs., **53** (10 Oct 1959) 18004

The effect of substituents in the 4- and 5-positions of 2-aminothiazole on the colour of the derived disperse dyes is discussed. Substituents in the 4-position have little effect; in the 5-position deepening of the colour occurs in the order of increasing negativity of the substituent groups so that a 5-nitro group gives greenish-blues of good properties. Preparative methods, m.p's, and infrared absorptions of many of the intermediates are given. E.S.

The Linear Isomer of Indanthrone
W. Bradley and M. C. Clark

Chem. and Ind., (51) (19 Dec 1959) 1601–1602

The linear isomer of indanthrone, i.e. *N,N*-dihydro-2,3-6,7-diphthaloylphenazine—



was prepared by heating an intimate mixture of 2,3-aminobromoanthraquinone (100 g.) and anhydr. K_2CO_3 (50 g.) for 7 hr. at 270–290°C. The crude product (93% yield) was purified by successive treatments using conc. H_2SO_4, boiling pyridine, boiling water, and boiling acetone to give 23 g. of the pure isomer. Also, a 35% yield of the linear isomer was obtained by heating mixed 2,3-diamino- and 2,3-dibromoanthraquinones with K_2CO_3 at 250°C. but other methods, e.g. interaction of formamide and hystazarinquinone (Schiedt); 2,3-diaminoanthraquinone heated with phosphoric acid and the attempted extension of Bollert's reaction to 2,3-diaminoanthracene, failed or gave very poor yields. The properties of pure *N,N*-dihydro-2,3-6,7-diphthaloylphenazine were studied and compared with those of indanthrone. Thus, the linear isomer is reddish-brown (indanthrone, blue), has m.p. > 500°C. (470–500°C. decomp.) and absorbs 5–6% of its wt. of water (ca. 1%); it forms a K salt, is a stronger acid than indanthrone and is less easily dehydrogenated by HNO_3 to the azine. E.T.

Affinity of Direct Dyes for Cellulose
R. A. Boss *TAPPI*, **42** (July 1959) 185A–190A

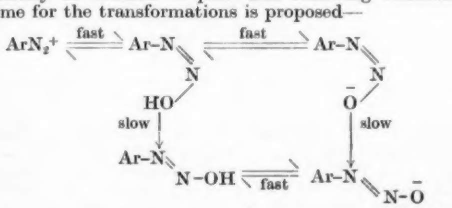
Azo dyes having amino groups show greater affinity for cellulose than those with phenol groups in the same position. Those with methoxy groups adjacent to azo groups have less affinity for cellulose than dyes otherwise having the same structure but not containing these groups, but more affinity than those having a methyl group in the same position. Phenolic groups adjacent to azo groups also reduce the affinity. Sulphonic acid groups adjacent to azo groups show less affinity than sulphonic acid groups in other positions. The higher the number of sulphonic acid groups, the lower the affinity. Most of the differences in affinity between azo dyes can be explained in terms of intramolecular and intermolecular hydrogen bonding. R.A.

Internuclear Cyclisation. XV—Catalytic Decomposition of Diazonium Chlorides prepared from *ortho*-Substituted 2-Amino-*N*-methylbenzanilides
D. H. Hey and R. A. J. Long
J.C.S., (Dec 1959) 4110–4113

Catalytic decomp. in acid media at room temp. by copper powder of the diazonium chlorides of the three 2-amino-*N*-methylbenzanilides which are separately substituted at the *ortho*-position with respect to the amino-group by CH_3, NO_2 or OCH_3, provide examples respectively of demethylation (I) and deamination (II) without phenanthridone formation (III), III without I and II, and concomitant I and II with III. H.H.H.

Diazonium Salt-Diazoate Equilibria
R. J. W. Le Fèvre, R. Roper, and I. H. Reece
J.C.S., (Dec 1959) 4104–4109

Equilibria reached in alkaline aq. media by the normal diazoates from aniline, *p*-chloroaniline, and sulphanilic acid, and by the isodiazoates from the three nitroanilines and sulphanilic acid, have been investigated photometrically in relation to pH. The following consistent scheme for the transformations is proposed—



H.H.H.

New Intermediates and Dyes. VII—Influence of the t-Butyl Group on the Properties of Azoic Dyes
V. Vassiliadis and A. T. Peters
J.C.S., (Dec 1959) 3928–3931

o-, *m*-, and *p*-t-Butylaniline are used as diazotisable amines, and also to prepare the coupling components (I) 3-hydroxy-*N*-*o*-, *m*-, and *p*-t-butylphenyl-2-naphthamides of 3-hydroxy-2-naphthoic acid (in boiling toluene in presence of PCl_3), for a series of azo dyes in substance and as azoic dyes on cotton. In general, the azoic dyes examined (from *N*-phenyl (Naphtol AS), *N*-*o*-tolyl (AS–D), and *N*-4-methoxy-2-methylphenyl deriv. (AS–LT) of 3-hydroxy-2-naphthamide and from I) containing the *p*-t-butyl group gave bright dyeings of good colour strength, very similar to those derived from the corresponding *p*-methyl analogues, but with a slight hypsochromic effect; the *o*-t- and *m*-t-isomers had similar characteristics. H.H.H.

Reductive Photo-bleaching of Eosine
Primary Processes indicated by the Flash Technique
S. Kato and M. Koizumi *Nature*, **184** (21 Nov 1959) 1620

Previous kinetic studies of this reaction (cf. Imamura and Koizumi, *Bull Chem. Soc. Japan*, **29** (1956) 899 and 913) indicated that a semiquinone radical of life $\nless 10^{-3}$ sec. is formed from the triplet state of dye and ethanol. Now, by the flash technique, it is found that in addition to the semiquinone, another intermediate is formed of life of the order of 10^{-3} sec. Only 12%, however, is permanently bleached, and a primary process, based on the formation of two transient species, is envisaged to account for this fact. In the presence of air, neither transient spectral change nor permanent bleaching was observed.

Effect of Added Substances on the Rate of Reductive Photo-bleaching
K. Uchida, S. Kato, and M. Koizumi
Ibid., 1620–1621

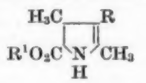
n-Hexene and cyclohexene increase the rate, whereas isopentane, *n*-hexane, benzene, and cyclooctatetraene have little effect. H.H.H.

Steric Effects in Di- and Tri-arylmethanes. I—Electronic Absorption Spectra of *o*-Methyl Derivatives of Michler's Hydrol Blue and Crystal Violet (C.I. Basic Violet 3); Conformational Isomers of Crystal Violet
C. C. Barker, M. H. Bride, and A. Stamp
J.C.S., (Dec 1959) 3957–3963

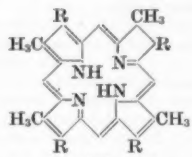
The first frequency absorption bands of the title substances show the expected reductions in frequency and intensity owing to the enforced rotation of the aryl rings. The *o*-positions of Michler's Hydrol Blue are not equivalent, and it is assumed that *o*-substituents take up less hindered "outside positions", so that the first frequency absorption band of the 2,2′,6,6′-tetramethyl deriv. shows, as expected, a much larger bathochromic shift and reduction in intensity. The 2-methyl, 2,2′-dimethyl, and 2,2′,2″-trimethyl deriv. of Crystal Violet show progressive bathochromic shifts and reductions in intensity, and the uniformity of the shift per CH_3 of the long-wavelength band suggests that the rotational adjustment necessary to accommodate the *o*-methyl groups is shared uniformly between the aryl rings. The conformation of the 2,6-dimethyl deriv. is discussed, and evidence against the existence of a conformational isomer of Crystal Violet is given. H.H.H.

Colouring Matters derived from Pyrroles. II—Improved Syntheses of Some Dipyrromethenes and Porphyrins
A. W. Johnson, I. T. Kay, E. Markham, R. Price, and K. B. Shaw *J.C.S.*, (Nov 1959) 3416–3424

A simple one-stage synthesis of pyrroles (I) (cf. *J.C.S.*, (1958) 4254) is now used for the preparation of the benzyl and t-butyl esters (I: $R^1 = CH_2C_6H_5$ or Bu^t) whose special properties have led to improved methods, now described, for preparing several dipyrromethanes which are readily converted to the corresponding dipyrromethenes. From the ester (I: $R = CH_2{\cdot}CH_2{\cdot}CO_2C_2H_5$, $R^1 = CH_2C_6H_5$), the esters of coproporphyrin (II: $R = CH_2{\cdot}CH_2{\cdot}CO_2H$) are conveniently synthesised.



(I)



(II)

H.H.H.

A Breakthrough in Pigment Technology—The New Yellow-Green Phthalocyanine
E. A. Wich *Amer. Dyestuff Rep.*, **48** (7 Sept 1959) 42–43

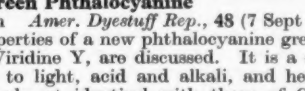
The properties of a new phthalocyanine green pigment, Heliogen Viridine Y, are discussed. It is a clean bright green fast to light, acid and alkali, and heat, and has properties almost identical with those of C.I. Pigment Green 7. It is available in several forms suitable for textile printing and padding and the mass coloration of viscose. Textile prints of good fastness to light, rubbing, chlorine, and dry-cleaning, are achieved. W.P.M.

Crystallography of Some Cyanine Dyes—I
P. J. Wheatley *J.C.S.*, (Nov 1959) 3245–3250

The cell constants and space groups of 3,3′-dimethylthiacyanine bromide and iodide, of 3,3′-diethylthiacarbocyanine bromide and iodide, and of their solvates are recorded. The structure of the unsolvated 3,3′-diethylthiacarbocyanine bromide is elucidated from two projections, and it appears that the cation is planar with the conjugated chain in the extended form, the sulphur atoms being *cis* with respect to this chain, while both methyl groups lie on the same side of the plane. The structure data are correlated with other properties of cyanine dyes.

II—Molecular and Crystal Structure of the Ethanol Solvate of 3,3′-Diethylthiacarbocyanine Bromide
Ibid., (Dec 1959) 4096–4100

The structure of the 1,1-solvate of ethanol and 3,3′-diethylthiacarbocyanine bromide—



has been determined by X-ray single-crystal methods from two projections. It was found that the crystals were actually a 1,1-solvate, and that they showed the same increase in internal disorder with time as the unsolvated crystals, and to about the same extent, they appear to be indefinitely resistant to spontaneous disintegration. The

conjugated chain is in the extended form with the sulphur atoms *cis* with respect to this chain. The methyl groups of the ethyl substituents lie on opposite sides of the cationic plane. The cation is not quite planar, the two halves being twisted through an angle of 8°. H.H.H.

Cyanine Dyes from 2-Methylacenaphthene-3′,4′:4,5-thiazole

A. V. Stetsenko

Ukrain. khim. zhur., **25** (May 1959) 623–6

2-Methyl acenaphthene-3′,4′,4,5-thiazole and its quaternary salts were synthesised and used to prepare a number of cyanine dyes. L.S.L.

Influence of Substituents on the Position of the Absorption and Fluorescence Spectra of Anthracene Derivatives

A. S. Cherkasov

Optics & Spectroscopy (English translation of *Optika i Spektroskopiya*), **6** (April 1959) 315–8

The influence of various substituents in various positions in the anthracene nucleus on the displacement of the absorption and fluorescence spectra compared with those of anthracene has been examined. With many poly-substituted anthracenes the value of the shift is equal to the sum of the shifts caused by each individual substituent. Deviations from this observed with some anthracene derivatives is caused by steric interactions of the substituents. C.O.C.

Peculiarities of the Luminescence of *ortho*-Substituted Aromatic Hydrocarbons. II—Fluorescence of the Methyl Esters of 2-Hydroxy and 2-Methoxy-naphthoic Acids

U. V. Naboikin, B. A. Zadorozhnyi, and E. N. Pavlova

Optics & Spectroscopy (English translation of *Optika i Spektroskopiya*), **6** (April 1959) 312–4

Appearance of three bands in the fluorescence spectrum of methyl 2-hydroxy-3-naphthoate results from intra-molecular hydrogen bonding. The spectrum of methyl 2-methoxy-3-naphthoate shows only a single band; this band is weakly perturbed by solvent effects. C.O.C.

Chromatography of Xanthene Dyes

K. B. Taylor *Nature*, **185** (23 Jan 1960) 243–4

Paper chromatography of commercial samples of Eosine Y (C.I. 45380), Erythrosine R (C.I. 45425), and Erythrosine B (C.I. 45430) showed that Eosine Y had two, Erythrosine R five, and Erythrosine B two coloured components. Investigation of the partial halogenation of Fluorescein (C.I. 45350) with Br and I in aqueous alkali showed that even when only 1 mol. of halogen had been added the reaction mixture contained five coloured components, viz. unreacted Fluorescein and the mono-, di-, tri-, and tetrahalogenated compounds. Further halogenation of the initial mixture resulted in gradual decrease of the proportion of components of high R_f value. The end product in each case had two coloured components which seemed to be identical with those of the commercial sample of Eosine Y and Erythrosine B respectively. Essentially similar results were obtained when halogenating [*P*]-tetrachlorofluorescein (C.I. 45366). A commercial sample of Rose Bengal Extra had two coloured components— tetra-iodo[*R*]-tetrachloro[*P*]-fluorescein (C.I. 45440) and the tri-iodo compound. Six samples of commercial Phloxine B (C.I. 45410) were more complex mixtures than the foregoing. Some of the components were identical with the products of bromination of [*P*]-tetrachlorofluorescein and in one case iodinated fluoresceins were also present. It is possible that the other components are derivatives of [*P*]-dichlorofluorescein the starting material for Phloxine [C.I. 45405]. In addition to the multiplicity of coloured components in these dyes, examination of the chromatograms under radiation revealed presence of a number of colourless compounds which showed brilliant fluorescence. This was especially marked in the case of derivatives of [*P*]-halogenated fluorescein. In some of the samples of Phloxine B as many as four such components were found. C.O.C.

Influence of Water Vapour on Absorption Spectra of Sublimated Layers of Dyes

L. A. Lyzina and A. T. Vartanian

Optics & Spectroscopy (English translation of *Optika i Spektroskopiya*), **6** (April 1959) 307–311

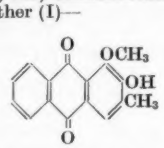
Dye layers obtained by sublimation *in vacuo* are usually amorphous. The dye aggregates in presence of water vapour, the degree of aggregation being of about the same order as in concentrated aqueous solution. With some dyes, e.g. Auramine (C.I. Basic Yellow 2), Methylene Blue (C.I. Basic Blue 9) and Thionine (C.I. Basic Blue 25), crystallisation occurs. In solid dye layers, depending on the state in which they are (vacuum, water vapour), different absorption layers can exist— "free" molecules, molecules under the substrate's influence, aggregated molecules, and microcrystallites. The shape of the absorption curve of the layer is determined by the relations between these absorption centres. C.O.C.

Naturally-occurring Quinones. III—A Synthesis of Digitolutein

J. C. Lovie and R. H. Thomson

J.C.S., (Dec 1959) 4139–4140

Digitolutein is a yellow pigment found in the leaves of the foxgloves *Digitalis lutea* Linn. and *D. purpurea* Linn. Degradative studies by Janot *et al.* (*Bull. Soc. chim. France*, (1955) 108) indicated the structure 3-methylalizarin 1-methyl-ether (I)—



which is now confirmed by the following synthesis— 3-methylcatechol is condensed with phthalic anhydride in fused $AlCl_3$-NaCl to give 3-methylalizarin which acetylates with boroacetic anhydride to 3-methylalizarin-2-acetate, and thence converted by methylation and subsequent hydrolysis to I. H.H.H.

Purification of Dyes by Thermal Diffusion

B. M. Bogoslovskii, B. M. Yavorskii, and A. D. Virnik

Zhur. priklad. khim., **32** (Oct 1959) 2225–9

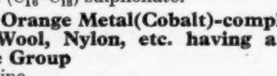
Apparatus for purifying dyes by thermal diffusion consists of two vertical, concentric, glass or stainless steel tubes. The outer tube is sealed at both ends and has at each end sampling taps for the soln. from the space between the tubes. Glass apparatus is heated by steam passing through the inner tube and metal electrically. The space between the tubes is filled with a dye soln. and heating of the internal and cooling of the external surface with cold water is commenced. The samples from both taps are taken and analysed. Increase in the conc. was found at the lower end of the column. The maximum change was reached after 1–2 hr. When the soln. analysed consisted of a mixture of dyes, more dye of lower mol. wt. was found at the bottom. When the mixture consisted of two dyes of equal mol. wt., the one composed of shorter molecules tended to collect at the bottom of the column. T.Z.W.

PATENTS

Red Monoazo Pigments

FBy *BP* 817,311

Yellowish red pigments of good fastness to light and solvents are prepared by diazotising amines—

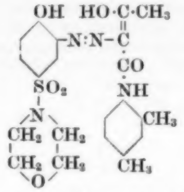


(R = CH_3 or OCH_3) and coupling with the *o*-toluidide or *o*-anisidide of 3,2-hydroxynaphthoic acid. These amines are prepared by condensing the alkali-metal salts of 4-hydroxyacetophenone or of methyl 4-hydroxybenzoate with 2-nitrotoluene-4-sulphonyl chloride, followed by reduction of the nitro group to NH_2. Coupling is best effected with a weakly acid fine suspension of the coupling component in presence of a surface-active agent, e.g. a sodium alkyl (C_{16}–C_{18}) sulphonate. E.S.

Yellow and Orange Metal(Cobalt)-complex Monoazo Dyes for Wool, Nylon, etc. having a Sulphonylmorpholine Group

General Aniline *BP* 825,606

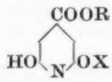
The Co-complexes of monoazo compounds 2-aminophenol-4-sulphonmorpholide (I) → acetoacetanilides give yellows of better wet fastness on wool and nylon than the corresponding dyes from 2-aminophenol-4-sulphonamide. Thus I is diazotised and coupled with acetoacet-2,4-xylidide, giving—



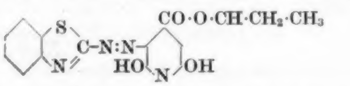
Refluxing with $CoCl_2$ in isopropanol gives the metal-complex, which is dried in presence of a dispersing agent, and gives orange on wool from a bath containing ammonium sulphate. E.S.

Benzthiazole-Monoazo-Isonicotinic Acid Compounds — Metallisable Disperse Dyes
Eastman Kodak Co. *BP* 817,374

Disperse dyes obtained by coupling diazotised 2-aminobenzthiazoles with isonicotinic acid derivatives—



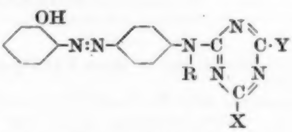
(R = H, Alk of 1–4 C, alkoxyalkyl of 3–6 C, or cyclohexyl; X = H or Alk of 1–4 C), may be metallised on the fibre. Or the metal-complexes prepared in substance may be dyed or printed on wool, nylon or polyacrylonitrile fibres or incorporated in fibre-forming spinning dopes. Thus citrazinic acid (2,6-dihydroxyisonicotinic acid) is boiled with *s*-butanol containing H_2SO_4 to give the ester, which is coupled with diazotised 2-aminobenzthiazole giving—



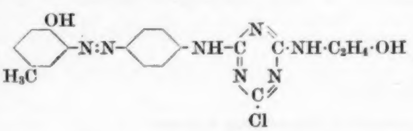
which dyes cellulose acetate bright orange, converted to bright bluish red by padding with aq. $Ni(SCN)_2$ and steaming at 5 lb. per sq. in. for 10–15 min. E.S.

Yellow and Orange Monoazo Disperse Dyes having a Halogenotriazinyl Group
ICI *BP* 825,377

Suitable *o*-hydroxy-*p*′-aminoazobenzenes, free of solubilising groups, are condensed with dihalogenotriazines to give disperse dyes—



(R = H or hydrocarbon radical which may be substituted; X = Hal; Y = subst. or unsubst. Alk or Ar, OH, NH_2, or an organic radical containing N, S, or O through which it is linked to the triazine ring) having good wet fastness on nylon. Alternative syntheses are described. Thus a slurry is prepared by stirring a solution of cyanuric chloride in acetone into water at $< 5°$C. Solutions of aq. Na_2CO_3 and of 4-amino-2′-hydroxy-5′-methylazobenzene in acetone are then slowly added, to give the dichlorotriazinyl derivative. Condensation at one of the Cl atoms with ethanolamine then gives—



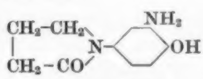
which dyes cellulose acetate and nylon yellow. E.S.

Reactive Disperse Monoazo Dyes for Nylon, etc.
ICI *BP* 825,912

Monoazo compounds free of solubilising groups and containing a primary or secondary amino group are condensed with 1 mol. of a cyanuric halide to give disperse dyes containing a dihalogeno-1,3,5-triazin-2-yl-amino group, which may be fixed on nylon, polyurethane, polyvinyl alcohol or modified polyacrylonitrile fibres by an alkaline aftertreatment. Thus 4-amino-4′-dimethylaminoazobenzene is condensed with 1 mol. of cyanuric chloride, and the product is applied to nylon at 95°c. from aqueous dispersion. Treatment in a hot aqueous solution containing 0·1% soap and 0·1% soda ash gives a yellow of very good fastness to washing. E.S.

Metallisable and Metal-complex Monoazo Dyes for Wool, etc., Having a Pyrrolidonyl Ring
FBy *BP* 826,207

oo′-Dihydroxymonoazo dyes prepared by diazotising *o*-aminophenols having a pyrrolidonyl substituent and coupling with an *o*-coupling naphthol or pyrazolone may be metallised with Co or Cr in substance or in the dyebath. Thus *p*-aminophenol is condensed with γ-butyrolactone, and the product is nitrated and reduced to give 2-amino-4-pyrrolidonyl-(1′)-phenol—



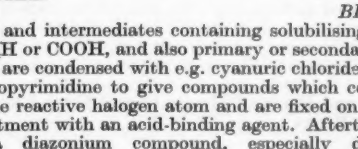
This is diazotised and coupled with β-naphthol to give the monoazo compound. Stirring at 85–90°c. with aq. $K_2Cr_2O_7$ and glucose in presence of NaOH gives the 1:2 Cr-complex which dyes wool reddish dark blue from a neutral or weakly acid bath. E.S.

Water-repellent Monoazo Dyes for Staining Wood
Midland Chemical Corp. *BP* 825,857

Monoazo dyes having 1 or 2 alkyl or aliphatic acyl radicals of 8–12 C attached through a CH_2 or CO group to an aryl residue, e.g. β-naphthylamine→2,4,6-trihydroxyphenyl-3-nonyl ketone, stain wood from solution or dispersion in e.g. mixtures of glycol ethers, without raising the grain, and impart resistance to moisture. E.S.

Yellow and Orange Reactive Pyrazolone Monoazo Dyes for Cellulose
ICI *BP* 826,405

Monoazo dyes containing attached to a triazine ring 2 Cl atoms and the residue of an amino derivative of 4-benzeneazo-1-phenyl-3-methyl(or carboalkoxy, or carboxy)-5-pyrazolone, and which contain 2 solubilising (SO_3 or COOH) groups, have good solubility and are readily fixed on cellulose by treatment with an acid-binder. Thus the monoazo compound aniline-2,5-disulphonic acid→1-*m*-aminophenyl-3-methyl-5-pyrazolone is condensed with 1 mol. of cyanuric chloride to give the yellow reactive dye.



E.S.

Coloration of Cellulose by Application of Reactive Dyes and Intermediates Aftertreated with Diazo Compounds
ICI *BP* 825,771

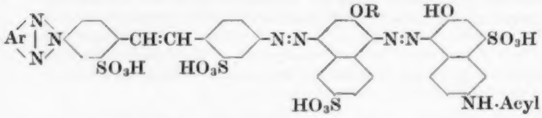
Dyes and intermediates containing solubilising groups, e.g. SO_3H or COOH, and also primary or secondary amino groups, are condensed with e.g. cyanuric chloride or 2,4,6-trichloropyrimidine to give compounds which contain at least one reactive halogen atom and are fixed on the fibre by treatment with an acid-binding agent. Aftertreatment with a diazonium compound, especially diazotised 4-amino-2,5-dimethoxy-4′-nitroazobenzene (I), then develops or alters the colour. Hence 2-colour effects can be produced by suitable resist or overlapping printing processes.

Thus 1 mol. of the monoazo compound 2-naphthylamine-4,8-disulphonic acid→*m*-toluidine is condensed with 1 mol. of cyanuric chloride. Cotton limbric is padded with a 2% aq. solution of the dye so formed, dried, and immersed for 1 min. at 90–95°c. in 3% aq. NaOH containing 20% NaCl. After rinsing, immersing in cold aq. 0·2% acetic acid, again rinsing, and boiling for 2 min. in aq. soap and soda ash, the cloth is dried. A patterned

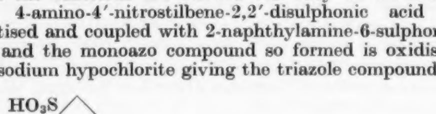
waterproof resist is then applied on both sides and the fabric is then dipped for 10 min. in a cold 2·5% aq. solution of the zinc chloride stabilised diazonium salt from I, to give a yellow patterned effect on a brown ground. E.S.

Green Metal(Copper)-complex Disazo Stilbene Dyes
Gy *BP* 825,431

Naphthotriazolyl derivatives of 4-aminostilbene are diazotised and coupled with 1-amino-2-alkoxynaphthalene-6-sulphonic acid, and the aminomonoazo compound so formed is diazotised and coupled with an *N*-acyl-γ acid to give disazo compounds—



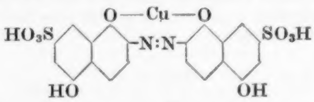
(Ar = naphthalene residue which may contain SO_3H groups and is bound to the N atoms by 2 adjacent C atoms; R = CH_3, C_2H_5, or $CH_2·COOH$), whose Cu-complexes dye cellulose greens of good light fastness. The order in which the reactions are carried out may be modified. Thus 4-amino-4′-nitrostilbene-2,2′-disulphonic acid is diazotised and coupled with 2-naphthylamine-6-sulphonic acid, and the monoazo compound so formed is oxidised with sodium hypochlorite giving the triazole compound—



The nitro group is reduced to amino with Fe and HCl, the product is then diazotised and coupled with 1-amino-2-methoxynaphthalene-6-sulphonic acid, and the aminomonoazo compound so formed is diazotised and coupled with *N*-benzoyl-γ acid. Boiling with aq. $CuSO_4$ gives the complex, which dyes cotton full green of good fastness to light and crease-resist finishing. E.S.

Green Metal(Copper)-complex Disazo and Trisazo Direct Dyes
FBy *BP* 818,008

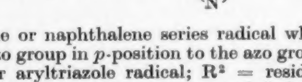
The Cu-complex monoazo compound—



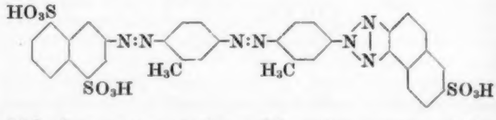
made e.g. by treating 2-diazo-5-*O*-benzenesulphonylhydroxy-1-naphthol-7-sulphonic acid with an ammoniacal cuprous salt by the method of *BP* 802,098 (J.S.D.C., **74** (Dec 1958) 875), is coupled with 1 or 2 mol. of the same or different diazo compounds of the benzene, naphthalene or stilbene series to give the title dyes. The disazo dyes formed when only 1 mol. of diazo compound is used may be converted into trisazo dyes on the fibre by aftertreating the dyeings with diazo compounds. Thus coupling 2 mol. of diazotised aniline with the above Cu-complex gives a green direct dye, whereas with 1 mol. of diazotised aniline a greenish blue is obtained, converted to yellowish green by coupling on the fibre with diazotised *p*-nitroaniline. E.S.

Orange and Brown Polyazo Direct Dyes Containing Triazole Rings
Gy *BP* 824,327

An *o*-aminoazo group in suitable polyazo compounds is oxidised, e.g. with air in presence of ammoniacal $CuSO_4$ or with hypochlorites, to give the title dyes, of formula—



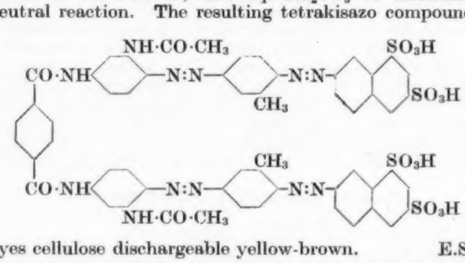
(R^1 = benzene or naphthalene series radical which may have an arylazo group in *p*-position to the azo group, or an arylthiazole or aryltriazole radical; R^2 = residue of *p*-coupling primary amine of benzene or naphthalene series; R^3 = residue of *p*-coupling primary amine of benzene series; R^4 = isocyclic or heterocyclic radical bound by adjacent C atoms to the triazole ring; 2–5 SO_3H groups are present). Thus the aminotrisazo compound 2-naphthylamine-4,8-disulphonic acid→*m*-toluidine→*m*-toluidine→2-naphthylamine-6-sulphonic acid is boiled with ammoniacal $CuSO_4$, giving—



which dyes cotton dischargeable yellow orange of high light fastness. E.S.

Yellow, Orange, and Brown Tetrakisazo Direct Dyes
Gy *BP* 817,871

Two mol. of suitable aminodisazo compounds are condensed with 1 mol. of a benzene-*p*-dicarboxylic acid halide to give the title dyes. Thus to a solution of the aminodisazo compound 2-naphthylamine-6,8-disulphonic acid→*m*-toluidine→*m*-aminoacetanilide in aq. Na_2CO_3 there is run in at 20°C. a solution of terephthaloyl dichloride in acetone, and aq. Na_2CO_3 to maintain a neutral reaction. The resulting tetrakisazo compound—



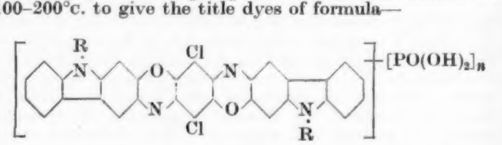
dyes cellulose dischargeable yellow-brown. E.S.

Aminoanthraquinones— Dyes for Polyacrylonitriles
BASF *BP* 824,530

Aminoanthraquinone carboxylic acid amides, the amido N atom of which is substituted by a radical containing a tertiary amino group, dye polyacrylonitriles from acid baths, in presence of dispersing agents and electrolytes if desired. The second H atom on the amide N atom may be replaced by Alk or Ar groups. Thus 1-aminoanthraquinone-2-(carboxylic acid *p*-diethylaminomethylanilide) gives reddish orange, and 1,4-diaminoanthraquinone-2-(carboxylic acid dimethylaminoethylamide) gives reddish-blue from dispersions containing acetic acid and sodium acetate. E.S.

Phosphonated Dioxazines— Blue Vat Dyes for Nylon
General Aniline *BP* 824,585

Suitable dioxazine dyes are dissolved in tetraphosphoric acid (P_2O_5 in orthophosphoric acid) and heated to 100–200°C. to give the title dyes of formula—

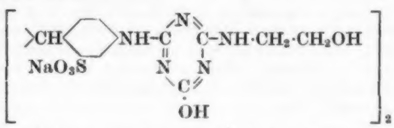


(R = H, Alk, cycloalkyl, Ar, aralkyl, etc.; *n* = 1 or 2). Thus 1 mol. of chloranil is condensed with 2 mol. of 3-amino-9-ethylcarbazole, and the product is ring-closed in presence of benzenesulphonyl chloride to give the dioxazine. Phosphonation is effected by dissolving in 83% tetraphosphoric acid and heating to 160°C., giving the product in which R = ethyl; *n* = 1, which dyes nylon bright blue from a vat containing pyridine and sodium hydrosulphite. E.S.

Fluorescent Brightening Agents
Fran *BP* 825,751

Compounds of formula—

(X = H or Alk; Y = acylamino mono-subst. ureido group; S^1 and S^2 = sulphonic or carboxylic groups) are fluorescent brightening agents particularly applicable to cellulosic materials. Thus—



exhausts on to cotton in 15 min. at 35–40°C. The treated fabric remains white even when laundered in presence of perborates or hypochlorites. C.O.C.

Phthalocyanine Pigments—Improvements in Physical Form
Société Nouvelle de Chimie Industrielle "Le Pont-du-Risse" *BP* 824,558

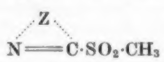
Crude phthalocyanine pigments are dissolved in sulphuric acid of > 70% concentration containing a glycol and preferably also a halogenated hydrocarbon, and precipitated by pouring into vigorously stirred water to give pigments of good colour strength and stability. Thus hexylene glycol (200 g.) is stirred into sulphuric acid 66°Bé. (1 kg.) at < 30°C., and a mixture of crude copper phthalocyanine (250 g.) with *o*-dichlorobenzene (125 g.) is added at < 40°C. After stirring for 3 hr. and standing for 12–15 hr., the mixture is poured into water (15 l.) at 60°C. The precipitated pigment is filtered, washed, steam-distilled to remove *o*-dichlorobenzene, dried, and ground. On heating in xylene at 130°C. for 1 hr. it retains its colour strength, whereas a conventionally-treated copper phthalocyanine in the α-form loses half its colour strength. E.S.

Halogenation of Phthalocyanines
General Aniline *BP* 818,831

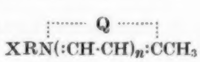
Halogenation is more readily controlled if the phthalocyanine is treated with Cl and/or Br in a fluid melt of anhydrous $AlCl_3$ and an oxide, bromide, chloride, oxybromide or oxychloride of sulphur at 60–200°C. and under atmospheric pressure. The products after isolation need no further conditioning to make them commercially useful. They are yellower than similar products made by other processes. C.O.C.

Cyanine Bases
Kodak *BP* 818,234

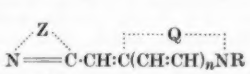
Condensing a compound of formula—



(Z = atoms to complete a benzthiazole, naphthothiazole or benzoxazole) with one of formula—



(R = Alk; X = anion; Q = atoms to complete a quinoline nucleus; *n* = 0 or 1) yields a dequaternised cyanine dye of formula—



Thus 2-benzothiazolylmethylsulphone condensed with 4-methylquinoline dimethyl sulphate yields 2-(1-methyl-4-quinolylidene)-methylbenzothiazole. C.O.C.

Vat Dyes of Fine Particle Size
Allied Chemical Corpn. *USP* 2,893,994

An aqueous alkaline solution of the leuco dye is formed into fine droplets which are then brought into contact with a liquid oxidising medium and the resulting fine precipitate recovered. By this means pigments are obtained whose particles are of uniform size, usually about 0·5 μ. They have better colour value, deeper mass tone and a clearer hue than similar products obtained by conventional means. C.O.C.

Stable Aqueous Dispersions of Water-insoluble Dyes
Commonwealth Engineering Co. *BP* 818,750

Carboxymethyldextran derived from a water-soluble native, unhydrolysed dextran and containing on average 1·0–3·0 carboxymethyl groups per anhydroglucopyranosidic unit has remarkable capacity for increasing the viscosity of water. This makes them of excellent use as stabilisers for aqueous dispersions of water-insoluble dyes. C.O.C.

Laundry Blue
Pennsalt Chemicals Corpn. *USP* 2,893,818

A mixture of sodium fluosilicate, C.I. Acid Blue 22 or C.I. Acid Violet 17, and 0·1–3·0% of Na_2CO_3, NaOH, Na orthosilicate, Na metasilicate, Na pyrophosphate or Na tetraborate when used in the final sour in laundering does not result in blue specks or streaks forming upon ironing. C.O.C.

Carbon Black (C.I. Pigment Black 6 and 7) Having Good Flow Characteristics
J. M. Huber Corpn. *USP* 2,893,887

Treating Carbon Black with an alkaline earth mahogany sulphonate yields a dry powder having enhanced flow-imparting characteristics. C.O.C.

Iron Blue (C.I. Pigment Blue 27) Composition for use in making Carbon Paper
California Ink Co. *USP* 2,893,886

The wet pigment is treated with an oil-soluble, water-insoluble long chain alkyl oxazoline or imidazoline and a non-drying oil. This results in rapid formation of oil globules containing dispersed Iron Blue which settle out of the water and so assists separation of water from the mixture. After the water has been separated, molten wax is added to produce a flowable mixture which solidifies upon cooling. This solid is then flaked to yield a product which readily disperses when used in the manufacture of transfer inks. C.O.C.

Silicon Dioxide (C.I. 77811)
B. F. Goodrich Co. *BP* 819,165

Apparatus for producing and oxidising silicon monoxide to solid amorphous silicon dioxide suitable as a rubber pigment. C.O.C.

Self Luminous Compositions
Brandhurst Co. *BP* 818,108

A mixture of a luminescent compound and an artificial radioactive isotope of the transuranic elements and emitting mainly α-radiation and little or no β-radiation has a level of radiation which is not dangerous nor does it give off radon. Thus a mixture of a ZnS/Cu phosphor and Americium 241 emits yellowish green light and only 7% of the radiation given off by a composition activated by radium. C.O.C.

Some Recent Advances in the Chemistry and Biochemistry of Commercially Important Condensed Tannins (III p. 190)
Adsorption of Driers by Titanium Dioxide (C.I. Pigment White 6) and Carbon Black (C.I. Pigment Black 6 and 7) (V p. 198)

V—PAINTS; ENAMELS; INKS

Pigment Dispersion in Szegvari Attritor—II
CDIC Paint & Varnish Production Club
Official Digest Fedn. Paint & Varnish Prod. Clubs, 31 (Nov 1959) 1374–6

Experiments using rutile TiO_2 (C.I. Pigment White 6), medium chrome yellow (C.I. Pigment Yellow 34), ferrite yellow (C.I. Pigment Yellow 42), and Lamp Black (C.I. Pigment Black 6) as pigments and a short oil soya alkyd as vehicle definitely confirmed that the Szegvari Attritor is excellent for rapidly dispersing pigments. C.O.C.

Predicting the Oil Absorption and Critical Pigment Volume Concentration of Multicomponent Pigment Systems
Philadelphia Paint & Varnish Production Club
Official Digest Fedn. Paint & Varnish Prod. Clubs, 31 (Nov 1959) 1490–1530

The spatula rub-up method for determining the oil absorption of a pigment can be used to obtain significant and useful information on fundamental pigment–vehicle relationships. With some training and care, operators can reproduce oil absorption values within rather narrow limits. There is an individual operator bias, readily determinable, which used to correct oil absorption values determined by him, markedly improves the general usefulness of oil absorption data. Oil absorption values of

pigment mixtures plotted against pigment composition produce curves not straight lines; pigment packing is indicated, the degree of pigment packing being the greater, the greater is deviation from a straight line. Pigment packing effects are shown by pigment mixtures whose components differ markedly in particle size. Pigments of about same average size and size range show no packing effect. Most coarse extender pigments can be treated as if they do not pack, probably because they have such a wide range of particle size that by themselves they already show a high degree of packing which obscures any additional packing, if any, caused by adding another pigment. Acicular pigments behave as if they have a wide range of particle size. Packing of fine pigments, e.g. white hiding pigments, is constant irrespective of the extender present. There is some evidence that these packing effects are directly or indirectly responsible for some important paint and film properties. The oil absorption of two component systems can be described adequately by a polynomial equation of at most the third degree. It is possible to assign to hiding and extender pigments oil contribution factors which, given the composition of a pigment mixture, permit calculation of the oil absorption and critical pigment volume concentration of multi-component systems. C.O.C.

Adsorption of Driers by Titanium Dioxide (C.I. Pigment White 6) and Carbon Black (C.I. Pigment Black 6 and 7)
Philadelphia Paint & Varnish Production Club
Official Digest Fedn. Paint & Varnish Prod. Clubs, **31** (Nov 1959) 1475–1489

Titanium dioxide and Carbon Blacks adsorb naphthenate driers. The readily accessible pigment surface is satisfied in a very short time, and the steady state adsorption proceeds at a very low rate. Weightwise and molewise Carbon Blacks adsorb larger amounts of Pb than of Mn, Ca or Co. Molewise TiO_2 adsorbs Ca the most. "Modified TiO_2", now readily available, adsorbs less drier than does the unmodified pigment. Either the drier does not lose its catalytic activity by being adsorbed by pigments and/or this adsorption is a fully reversible process. The naphthenate driers are adsorbed as such and do not form a complete monomolecular layer but cover only the more active areas on the pigment surface. C.O.C.

Varnish Films based on Colloidal Dispersion of Carbon Black
L. V. Rozental' and G. I. Burdÿguna
Zhur. priklad. khim., **32** (Sept 1959) 2080–2084

Varnish films, based on cellulose acetophthalate, on nitrocellulose and cellulose triacetate, are not fast to dilute alkali. Perfectly stable suspensions of Carbon Black in acetophthalate can be produced without use of stabilising or dispersing agents. The stability of these suspensions and their adhesive properties depend upon the content of the phthaloyl and free carboxyl groups in the cellulose acetophthalate, the properties of Carbon Black used, and its degree of disaggregation during the dispersion and upon the composition of the dispersing medium. T.Z.W.

Some Laboratory Techniques for Colour Control in Paint Production
New York Paint & Varnish Production Club
Official Digest Fedn. Paint & Varnish Prod. Clubs, **31** (Nov 1959) 1377–1394

An account of improved techniques in control procedures, maintenance of standards and methods of accelerating tests for colour matching. 14 references. C.O.C.

PATENTS

Dispersing Carbon Black (C.I. Pigment Black 6 and 7) in Liquids
Columbian Carbon Co. *BP* 818,489

Apparatus for treating a mixture of the pigment and liquid to get uniform dispersion before passing it through a conventional colloid mill. This preliminary treatment prevents clogging of the colloid mill. C.O.C.

Printing Inks for Plastic Foils
Deutsche Gold- und Silberscheideanstalt *BP* 818,736

Modification of *BP* 759,232 (J.S.D.C., **73** (1957) 36). Addition of an oxide aerogel of particle size $\not> 0{\cdot}05\,\mu$. improves adhesion to plastic foils of any kind of printing ink. C.O.C.

Carbon Paper
Kee Lox Manufacturing Co. *USP* 2,893,890

The substrate is coated with a mixture of a plastisol dispersion resin, e.g. a dispersion of poly(vinyl chloride) plasticiser, non-plasticising non-volatile diluent colour carrier and a colorant. Such a mixture has low viscosity at room temperature but on heating fuses to form a firm, hard non-tacky film. C.O.C.

Vanadium Pentoxide as Whitening and Opacifying Agent for Enamels
Union Carbide Corpn. *BP* 826,306

Vanadium pentoxide is an excellent whitening and opacifying agent for enamels composed of PbO, SiO_2 and B_2O_3. C.O.C.

Iron Blue (C.I. Pigment Blue 27) Composition for use in making Carbon Paper (IV p. 197)
Self Luminous Compositions (IV p. 197)

VI—FIBRES; YARNS; FABRICS

Black Spot Defects in Cotton Fabrics
R. Schneider
Bull. Inst. Text. France, (82) (June 1959) 105–110

The principal causes of black spots in cotton fabrics are discussed and illustrated. These are (*a*) extraneous vegetable material, (*b*) oil spots, (*c*) tar spots, (*d*) rubber fragments from roller coverings, and (*e*) aggregates of fungal spores. The last case is discussed in some detail. J.C.F.

Effect of Soil on the Photochemical Degradation of Cotton
M. A. Morris and B. Wilsey
Textile Res. J., **51** (Dec 1959) 971–4

Cotton yarns impregnated with an airborne soil and then exposed to light from a carbon arc showed accelerated photochemical degradation measured by fluidity and breaking-strength tests. Yarns impregnated with a ground soil and a lignin derivative of the ground soil showed no such photosensitising action. C.O.C.

Dry Weight of Wool
I. C. Watt, R. H. Kennett, and J. F. P. James
Textile Res. J., **51** (Dec 1959) 975–981

When drying wool *in vacuo* the time needed to reach equilibrium weight decreases with increase in temperature up to 140°C. The equilibrium weight obtained *in vacuo* is less than the weight obtained in air under the same conditions. The activation energy of drying increases markedly at low regains. Comparison with partly acetylated wool suggests that drying wool at low regains involves removal of water from hydrophilic sites in the fibre. C.O.C.

Change in Stress on Wetting and Drying Wool Fibres
M. Feughelman *Textile Res. J.*, **51** (Dec 1959) 967–970

When a wet wool fibre is stretched to a fixed extent, kept stretched for some time and then dried, stress in the fibre is caused. This stress is independent of how long the fibre was stretched provided it is at least 1 min. and is also independent of a number of chemical and physical modifications to various fibres. The rise in stress is dependent on the degree of stretch and increases to a maximum at about 30% extension. Between 30 and 50% extension no increase in stress was noticed. Drying the fibre while stretched introduces strained hydrogen bonds which cause the rise of stress on drying. C.O.C.

Chlorophyll Contamination of Wool and its Effect on the Lightfastness of Dyeings
AATCC Continuous Wool Scouring Processes Subcommittee, Technical Committee on Research
Amer. Dyestuff Rep., **47** (1958) 118–124

Contamination of raw wool by chlorophyll will cause pastel dyeings subsequently applied to it to rapidly fade towards red. A method to determine presence of troublesome amounts of chlorophyll in raw wool is described as well as a way of removing most of the chlorophyll during the initial processing of the wool. Bile may also be a contributing factor in "red fade". Bile usually contains two pigments both formed by decomposition of haemoglobin. One is the greenish biliverdine which

predominates in sheep bile and the other is the yellowish-brown bilirubin. C.O.C.

Effect of Substitution by Iodine in the Solubility of Wool in Urea-Bisulphite
M. Levau, M. Caillet, and N. Demonmerot
Bull. Inst. Textile France, **84** (Oct 1959) 17–32
Substitution by iodine in the phenolic portion of the tyrosine residue in keratin results in marked insolubility of the keratin in urea-bisulphite. The implications of this from the viewpoint of wool structure are discussed. C.O.C.

Formation of Chelate Bonds
N. Hojo *J. Soc. Textile Cellulose Ind. Japan*, **15** (March 1959) 198–9

VII—Activation Energy of Adsorption of Mercury by Wool
The degree of chelate formation is proportional to the adsorption of heavy metallic ions; hence the rate of adsorption of Hg by wool should be a measure of the rate of chelation. This can be fitted to the equation $-\frac{dx}{dt} = K/x^n$ where x is the fraction of Hg adsorbed in time t, or to the equation $(n + 1) \log x = \log t + c$. Experimental results show a linear relation between $\log x$ and $\log t$ as predicted. The calculated activation energy is 6·8 kcals/mole between 10 and 20°c., and 9·6 kcals/mole between 20 and 30°c.

VIII—Effect on Strength of Silk
Ibid., 199–202
The fibre strength is greatly increased by the adsorption of the maximum amount of Cu. L.P.

Cross-linking of Wool by Aldehydes. II—Mechanism of Cross-linking
G. Decroix, G. Mazingue, and M. Van Overbèke
Bull. Inst. Text. France, (84) (Oct 1959) 33–47
Formaldehyde is a satisfactory agent for cross-linking wool. For aldehydes of the same chain length, the unsaturated are more reactive than the saturated, the effectiveness of the latter being negligible. Cross-linking results from the aldehyde reacting with two amino groups present either as free amino groups at the end of or situated along polypeptide chains or in salt linkages, the acid groups of the latter remaining unaffected. C.O.C.

Influence of Light and Weather on Strength of Polyamide Fibres, Wool and Silk
D. N. Griboedov, V. F. Androsov, and É. R. Tsirule
Tekhnol. tekstil. prom., **3** (10) (1959) 112–120
Dyed and undyed fibres were exposed to sun and weather. The dyes used were Chrome Brown K and Acetate Brown. The effect of afterchroming was also examined. Undyed fibres were found to be more susceptible to weather damage. The protective effect of the dyes was more pronounced in the case of synthetic fibres, specially delustred ones. Steam setting, also, improved resistance to light and weather. L.S.L.

Acetate—A Basic Fibre for Bonded Fibre Fabrics
J. L. Barach and H. W. Coates
Amer. Dyestuff Rep., **48** (1 June 1959) 43–9
Production, uses, and potentialities of bonded fibre fabrics are described and discussed. W.P.M.

Cellulose Acetate Succinamates
J. E. Kiefer, G. P. Tovey, and J. R. Caldwell
Ind. Eng. Chem., **51** (Dec 1959) 1481–2
N-substituted succinamic acids react almost quantitatively with cellulose in presence of a simple acid anhydride. This reaction offers a simple method for introducing various *N*-alkylamido and *N*-arylamido groups into cellulose esters. Thus addition of *NN*-dimethylsuccinamic acid to a cellulose acetylation mixture results in a cellulose acetate having affinity for acid dyes. The *NN*-dimethylsuccinamate group has little effect on the solubility or melting properties of the cellulose acetate, however, replacing the succinamic methyl groups by larger alkyl groups or by aryl groups results in a cellulose acetate of increased solubility in organic solvents and lower m.p. C.O.C.

Reaction of Diazomethane with Silk Fibroin. II—Methylation in Acetone Solution
T. Kuwamura, Y. Nakamura, H. Ito, and M. Negishu
J. Soc. Textile Cellulose Ind. Japan, **15** (March 1959) 191–6
Acetone is a more effective methylating medium than ether because of its higher b.p. The moisture content of silk affects the degree of methylation, the optimum value being 4%. Methylation has no effect on external appearance or mechanical properties but improves resistance to degradation by light. L.P.

Migration of Liquids in Textile Assemblies
F. W. Minor, A. M. Schwarz, E. A. Wulkow, and L. C. Bucker

Part II—Wicking of Liquids in Yarns
Text. Research J., **29** (Dec 1959) 931–9
Mathematical.

Part III—Behaviour of Liquids on Single Textile Fibres *Ibid.*, 940–9
An account of work done on a variety of fibres with single drops of liquids having no swelling action. C.O.C.

Drying a Mass of Hygroscopic Fibres by Forced Convection of Air—Some Physical Aspects
J. G. Downes and G. B. McMahon
Text. Research J., **51** (Dec 1959) 1006–1010
In drying a uniform mass of fibres by forced convective air flow through the mass, a "drying front" proceeds through the mass in the same direction as, but much more slowly than, the airflow. Therefore, if uniform drying is to be obtained, drying must continue until the front has emerged from the downstream face of the mass of fibres. Air of appropriate R.H. must be used to leave the fibres at the desired regain; reversal of airflow direction is undesirable on grounds of efficiency. Calculations made of the capacity of air to remove water from a mass of wool fibres to leave them at 4, 8, 12, and 16% regain show that except for fibres to be left at 4% regain, the capacity for water removal depends very little on the initial temperature of the air (in the range 30–110°c.). C.O.C.

PATENTS

Regenerated Zein Fibres
Virginia-Carolina Chemical Corpn. *BP* 817,724
An aqueous solution of zein containing 0·5–10·0% of HCHO on the wt. of zein and of pH 11·0–12·5 is extruded into a solution of 1–3% H_2SO_4, 2–10% HCHO, 1–6% $(NH_4)_2SO_4$, and 0·1–0·5% "goulac" at 80–100°F. (goulac is the trade name for a lignin preparation derived from sulphite waste liquor.) The resulting filaments are made into a tow which is passed for 30–180 min. through a direct chamber maintained at high humidity and 80–100°F. It is then stretched, and while under tension impregnated with an aqueous solution of 3–10% H_2SO_4 and 3–10% HCHO which is at least 90% saturated with NaCl. The impregnated tow is then relaxed and kept in a chamber at 90% R.H. at 110–140°F. for 30–120 min. Finally it is washed, baked, e.g. at 300°F., rinsed and dried. This yields fibres of high quality as regards dry and wet strengths, shrinkage, dyeing properties, etc. C.O.C.

Increasing the Affinity of Regenerated Zein Fibres for Acid Dyes
Virginia-Carolina Chemical Corpn. *BP* 817,723
An alkaline dispersion of zein, containing 0·5–10·0% of HCHO on the wt. of zein, is extruded into an acid bath and the resulting filaments treated in aqueous formaldehyde at pH 1–3 and 30–55°c., washed and stretched. They are then treated in aqueous acid at pH 0·5–5·5 in absence of formaldehyde and at $\nless$ 150°F. long enough to improve their affinity for acid dyes and finally all acids and salts are washed out of them. The resulting filaments retain their increased affinity for acid dyes even after being kept for years. C.O.C.

Mass-coloured Acrylic Fibres
FBy *BP* 817,614
The acrylonitrile polymer is dyed by adding to the spinning solution a basic dye soluble in the solvent and having affinity for the polymer, e.g. the dye obtained by condensing 1,3,3,-trimethyl-2-methylenindoline-ω-aldehyde with 6-amino-2-methylbenzthiazole. C.O.C.

Acrylic Fibres of Good Dyeing Properties
Dow Chemical Co. *BP* 817,617
Acrylic fibres containing 1–12% by wt. of a vinyl lactam polymer that was initially formed as a polymer of Fikentscher K value ≮ 40, e.g. polyvinylpyrrolidone, are readily dyed by conventional methods with acid, vat, disperse, direct, azoic, and sulphur dyes. C.O.C.

Some Factors Involved in Wash and Wear Wool (X p. 204)

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Effect of Pulp History on Pulp Response during Hypochlorite Bleaching
J. C. Paulson *TAPPI*, **42** (Aug 1959) 683–687
The pulp–hypochlorite reaction is considered a cellulose depolymerisation reaction in which lignin and hemicellulose compete for the hypochlorite. The reaction comprises an initial rapid stage, depending on the amount of lignin present and only affecting cellulose D.P. slightly, and a slow reaction during which pulp fluidity increases as a linear function of the amount of bleaching agent consumed. R.A.

Distribution of Oxidant Consumption in Bleaching
J. H. E. Herbst and H. Krässig
TAPPI, **42** (Aug 1959) 660–664
In the degradation of cellulose, the function $1/P_j - 1/P_o$ is approx. a the fraction of bonds broken, when P_j and P_o are the D.P. at time j and at the start respectively. The curve obtained on plotting this function against bleach consumption has a long straight portion, the intercept of which with the bleach consumption axis is a measure of the residual lignin content. The slope of the straight portion decreases with residual lignin content and with increasing hemicellulose content. Temp., choice of hypochlorite or peroxide, rate of reaction, and pH have no appreciable effect on the intercept, while hypochlorite, high reaction rate, and low pH give high slopes. R.A.

Wool Carbonising—Effects of Acidity and Moisture Content
G. Wibaux, G. Mazingue, and M. Van Overbèke
Bull. Inst. Text. France, (83) (Aug 1959) 85–98
Chemical degradation of carbonised wool, as measured by alkali solubility, increases directly with the amount of residual acid in the wool, whereas the effect on mechanical properties is much less marked. By contrast, too high a water content of the wool entering the carbonising oven can produce drastic reduction in mechanical strength without affecting alkali solubility. These observations justify application of a pre-drying treatment before baking, and emphasise the inadequacy of alkali solubility alone as a criterion of damage caused by carbonising.
J.C.F.

Effect of Phosphates and Silicates on Raw Silk. VI—Effect of Condensed Phosphates in Bleaching
E. Ohmura, A. Hirata, and M. Kobayashi
J. Soc. Textile Cellulose Ind. Japan, **15** (March 1959) 187–190
Phosphates in general have a stabilising effect on aq. H_2O_2 and hydrosulphite, slight individual temperature variations being possible. Metaphosphate glass has the greatest effect upon hydrosulphite and pyrophosphate (< 100°c.) on H_2O_2. The weight of sericin, W, dissolved by hydrosulphite is proportional to the amount of hydrosulphite present when the reaction time is less than 30 min.; this is reversed above 60 min. With stabilised hydrosulphite, W is proportional to the weight of stabilising agent and length of treatment, but with stabilised H_2O_2, W is small. L.P.

Present-day Trends in Bleaching
B. K. Easton
Amer. Dyestuff Rep., **48** (24) (30 Nov 1959) 24–29
A review of current U.S. procedures and latest developments. Major emphasis is given to the bleaching of cotton–synthetic fibre blends as well as to the bleaching of all cottons. In cotton bleaching special attention has been directed toward open-width working where it is felt there is definite need for improvement in continuous open-width equipment and procedures. New-type pressure equipment, which may soon be available for laboratory testing, could meet this need. A modified method of open width bleaching in batches in the cold yields much improved absorbency. C.O.C.

Continuous Bleaching System
J. Dungler *Textil Praxis*, **14** (Aug 1959) 810–813
Describes the Dungler machinery and procedure developed for continuous bleaching of cotton fabric. Amongst the novel features is use of superheated instead of saturated steam as a heating medium in the reaction chambers. Not only is 100°c. readily attained but the metal parts are immune from corrosion as long as they do not come in contact with saturated steam. A typical installation for continuously treating cotton fabric consists of the following stages: desizing and caustic boil (impregnation and reaction chamber), wash off, souring, chlorite bleaching (impregnation and reaction chamber), neutralisation, and rinsing. Rate of production is over 100 yd./min. L.A.T.

Delignification of Flax by Aqueous Acid Sodium Chlorite
M. Heude and V. Bossuyt
Bull. Inst. Text. France, (82) (June 1959) 89–102
Effect of concentration, reaction time, and temperature on removal of lignin from flax fibres by aqueous acid sodium chlorite has been investigated. Even under severe conditions, when considerable breakdown of the cellulose occurs, complete removal of lignin is not attained, and under milder conditions about half the lignin remains insoluble. Previous extraction of pectic material does not influence the delignification process. The residual lignin, characterised by a low methoxyl content, does not inhibit extraction of hemicelluloses by cold conc. NaOH.
J.C.F.

Bleaching Treatments—Effect on Subsequent Bleaching of Linen Fabric
A. Parisot *Bull. Inst. Text. France*, (82) (June 1959) 59–87; (83) (Aug 1959) 7–24
Examination of successive samples of linen fabric subjected to one of twelve different commercial bleaching treatments, and then to accelerated chemical degradation treatment, led to the following conclusions— (*a*) there is close correlation between the mean D.P. of the cellulose and the Solubility Index (S.I.) of the fibre; (*b*) the variations of D.P. and S.I. with successive treatments are of the same mathematical form, but the parameters involved depend on the degree of polydispersity of the cellulose, which itself depends on the initial bleaching treatment; (*c*) there exists a proportionality relation between (initial D.P/mean D.P)–1 and the function Δ_R defined as $100\ (R_1-R_2)/R_2$ where R is the value of a mechanical property measured in the wet (1) and conditioned (2) state; (*d*) the mean D.P. value corresponding to $\Delta_R = 0$ depends on the particular initial bleaching treatment, and therefore on the degree of polydispersity. This limiting D.P. value appears to be influenced by the ratio of mechanical degradation to chemical degradation. When chemical degradation preponderates, this limiting D.P. value is about 600. An appendix describes a tentative standard method for determination of Solubility Index. J.C.F.

Influence of $Na_5P_3O_{10}$-$CaCl_2$-H_2O Phase Equilibrium on Laundering of Cotton Fabric
W. J. Diamond and J. E. Grove
Textile Res. J., **29** (Nov 1959) 863–872

Nature of Tenaciously Bound Soil on Cotton
W. C. Powe *Textile Res. J.*, **29**, (Nov 1959) 879–884
The major particulate materials causing soil build up on cotton fibres after repeated dry cleaning and laundering are clay minerals 0·02–1·0 μ. diameter. C.O.C.

Hank Mercerising
R. B. Vogel and H. Hölters
Textil Praxis, **14** (Sept 1959) 937–942
Machinenfabrik Gerber-Wansleben, Krefeld, have developed a new yarn mercerising machine. The hanks are not immersed but are sprayed with mercerising lye. It is claimed mercerising time is reduced by about 40%. Tests have shown that it is unnecessary to double mercerise hard-twisted ply yarns, satisfactory mercerising being obtained in one operation. L.A.T.

PATENTS

Bleaching Cellulosic Material with Hypochlorite
Nederlandse Organisatie voor Toegepast-Natuurwetenschappelijk Onderzoek ten Behoeve van Nijverheid Handel en Verkeer *BP* 822,974

Cellulosic material is rapidly bleached with hypochlorite if (1) the material is in continuous contact with hypochlorite, (2) the concentration of hypochlorite is kept very low, and (3) the bleaching liquor is alkaline. These conditions can be controlled by measuring the electric potential of the bleaching bath as in the region of very low hypochlorite concentrations in alkaline medium the electric potential is highly dependent on the concentration of active chlorine. C.O.C.

Bleaching Cellulosic Pulp
Scott Paper Co. *BP* 818,828

High density pulp is impregnated with hypochlorite solution under such conditions of duration and temperature that no bleaching action occurs. After this the temperature is immediately raised to effect bleaching action. When the desired brightness is obtained bleaching is stopped by drowning the bleached mass in water. C.O.C.

Wool Scouring
E. F. Drew & Co. *BP* 823,277

The wool is passed continuously and successively through a desuinting bowl, scouring bowl, and rinsing bowl. Water, preferably above room temperature, is fed into the desuinting bowl and into the scouring bowl at a temperature above that in the desuinting bowl. The scouring bowl is initially charged with 0·5–5·0 g. per litre of a non-ionic detergent, this concentration being maintained by continuous additions throughout the process. Water is fed into the rinsing bowl at a temperature between that of the desuinting and scouring bowls. This scours the wool with minimum of felting. C.O.C.

Europe's Model Textile Finisher (Process Control at the Royal Twentsche Steam Bleachery) (I p. 190)
Reclaiming Dry-cleaning Solvent (I p. 190)
Laundry Blue (IV p. 197)
Continuous Wet-processing of Cotton–Acrilan Work-clothing Fabrics (VIII this page)

VIII—DYEING

Substantivity and Affinity
J. Wegmann *Textil-Rund.*, **14**, (Nov 1959) 631–642

The distinction is first discussed between the conceptions of substantivity and affinity, where the former is held to refer to the fixation-capacity of a dye or other textile cpd. for a textile substrate when applied in a liquid medium, and the latter to the measure of the force with which the above substances are held by the substrate. It is emphasised how much confusion has arisen hitherto by not keeping these conceptions apart. The cases of direct, copper-complex, and vat dyes are then considered, and followed by those of azoic, reactive, acid, and disperse dyes. A classification is included of dyes with respect to the various affinity forces (ionic, dipole, dispersion, subsidiary valency, covalent-union, and mechanical). The conception of thermodynamic affinity only holds under equilibrium conditions, and it is then the difference in free energy of the dye in solution and on the fibre. 31 references. H.H.H.

Diffusion of Dyes
R. H. Peters and J. H. Petropoulos
Bull. Inst. Text. France (84) (Oct 1959) 49–68

The distribution curves obtained from microdensitometric measurements of cross-sections of dyed films of cellulose, acetate, nylon, and regenerated cellulose have been used to calculate the effect of concentration on the coefficients of diffusion. The results are discussed in light of the accepted theories of dyeing of these substrates. C.O.C.

Light-fastness of Selected Direct Colours on Cotton, Rayon, and Cotton–Rayon Blends
AATCC Delaware Valley Section
Amer. Dyestuff Rep., **47** (1958) 115–7

The fastness to light of direct dyeings on cotton–rayon blends is directly proportional to the amount of rayon in the blend. Bleaching before dyeing has significant effect on fastness to light. The fastness to light of dyeings obtained by padding and on the winch are the same, indicating that degree of penetration of the dye plays no part in fastness to light. Dyeings on mercerised material are faster to light than those on unmercerised. C.O.C.

Dyeing of Tufted Carpets
M. Peter, H. V. Schmidlin, and H. Stern
S.V.F. Fachorgan, **14** (July 1959) 407–425

Manufacture of tufted carpets has increased considerably in recent years, particularly in the U.S.A., where in 1958 tufted carpets were 61% of total carpet production. The pile yarn can be made from any one or a combination of the following fibres: viscose rayon, wool, polyamides, and acrylics. Loose stock, yarn and piece dyeing are practised, the latter requiring winches of special design and robust construction to allow handling pieces up to 18 ft. wide and about 120 yd. long, weighing 2–5 lb. per sq.yd. Cellulosic yarn may be dyed with substantive, vat, and reactive dyes, whilst for piece dyeing only selected substantive colours are suitable. Carpet yarn made from polyamide fibres may be dyed with acid, pre-metallised, and Elanyl (Ciba) dyes, and those made from polyacrylonitrile with basic and disperse dyes. Fastness requirements include light, dry cleaning, rubbing, shampooing, water spotting, and water-bound street dirt. L.A.T.

Continuous Wet-processing of Cotton–Acrilan Work-clothing Fabrics
AATCC South Central Section
Amer. Dyestuff Rep., **48** (22) (2 Nov 1959) 35–41

An account of procedures that have been developed, using conventional cotton processing equipment, to produce fabrics dyed equally as fast as cotton fabrics and of better resistance to abrasion, tearing, and acid. C.O.C.

Vat Dyeing of Zefran–Cotton Blends
R. L. Burgess
Amer. Dyestuff Rep., **48** (24) (30 Nov 1959) 19–23

Blends of cotton and Zefran acrylic fibre can be obtained in light to heavy dyeings with vat dyes at 120–180°F. Medium and heavy dyeings have to be carried out at 140–180°F. Light dyeings may require a retarding agent to prevent too much dye going on to the Zefran. The most effective agent yet found is 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane. The amounts necessary with various vat dyes are given and a list of vat dye combinations that yield solid dyeings on these blends when using pack machines or the pad–jig method. C.O.C.

Dyeing Wool below the Boil
C. H. A. Schmitt
Amer. Dyestuff Rep., **48** (7 Sept 1959) 40–41

Dyeings were carried out on wool at 165, 175, 185, and 212°F. at a dyebath pH of 5·8, using acid milling and neutral premetallised type dyes. In most cases brighter dyeings were obtained below the boil. At 185°F. good fastness to light and washing is achieved with only slightly less colour yield than at the boil but at 175°F. there was occasional loss of fastness. The results obtained with several dyes are tabulated. The process saves time and steam and gives wool which has a softer handle and is easier to wind and knit. W.P.M.

Demetallisation, Levelling, and Rechroming of Chrome-dyed Wool Pieces
H. E. Millson
Amer. Dyestuff Rep., **48** (7 Sept 1959) 47–58

Use of the sequestering agent Cyquest 40 (tetrasodium ethylenediamine tetraacetate) with certain acids enables removal of salts of many metals (including the "tramp" metals) even after the dye–metal–wool complex has been formed. Treatment with Cyquest 40, oxalic acid, and Na_2SO_4 has proved in mill practice to be an efficient method of demetallising and levelling uneven chrome mordant, metachrome, and afterchrome dyeings. C.O.C.

Accelerant Dyeing of Hydrophobic Fibres—Principles and Mechanisms
AATCC Piedmont Section *Amer. Dyestuff Rep.*, **48** (22) (2 Nov 1959) 23–34; (23) (16 Nov 1959) 37–45

Critical examination of the mechanism and principles involved in the action of carriers indicates that the carriers act within the fibre rather than in the dyebath. The dye molecules diffuse through "holes" formed as fibre polymer

interchain bonds dissociate under thermal agitation. The carrier is absorbed by the fibre and acts by partly replacing interchain bonds with more readily disrupted fibre-carrier bonds. With this increased mobility, the number of openings increases under the same thermal energy content resulting in a more permeable fibre and quicker diffusion of dye. Guiding principles for optimum use of carrier and a more objective insight into the mechanism are derived from basic experiments. Techniques needed in the investigation of these new approaches are described for: (1) Solubility of dyes in carriers, (2) Quantitative absorption of carrier by fibre, (3) Effect of surfactants and liquor ratio on carrier action, (4) Desorption of dye in presence of carrier, (5) Effect of pretreatment of fibre with carrier on subsequent dyeing rate, (6) Effect of carrier on water imbibition, (7) Migration of dye from carrier films, and (8) Physical effects of carrier on fibre. The principles established and the proposed mechanism have been successfully applied to answering 16 problems and questions confronting the practical dyer. C.O.C.

Dyeing Creslan and Verel Fibres
H. G. Fröhlich

S.V.F. Fachorgan, **14** (Aug 1959) 499–501

Creslan is a copolymer of acrylonitrile and acryloamide, and Verel a copolymer of acrylonitrile and vinyl chloride. Five classes of dyes are applicable to Creslan: acid, chrome, premetallised, basic, and disperse. Acid dyes are applied with 5% Glauber's salt and 0·5–2·0% acetic or formic acid. When the dyebath is about 80% exhausted at approx. 88–93°c., 2% H_2SO_4 is added and the bath raised to 96–97°c. With chrome and metal complex dyes the procedure is similar to that of wool dyeing. Basic and disperse dyes are applied at the boil, the former at pH 5·5–6·0, and the latter with aid of a suitable dispersing agent. Verel can be dyed with basic, disperse, and 1:2 metal complex dyes. With basic dyes the dyebath is set with 0·5% acetic acid, 0·3% Na acetate, and 0·5% Alkanol HCS (DuP). After dyeing for 60–90 min. at 82–88°c., 50% NaCl is added and the temperature maintained at 88°c. for a further 15 min. Disperse dyes are used with a suitable dispersing agent for pastel and medium dyeings. For darker dyeings addition of a carrier is required, e.g. 6% Verel Dyeing Assistant in presence of 2% acetic acid. Pre-metallised dyes are applied with 3% Verel Dyeing Assistant and 5% NH_4 acetate. The light and washing fastness of the basic and premetallised dyes is good, that of disperse dyes only moderate. L.A.T.

Sorption of Congo Red by Polyvinyl-Formal
K. Fujiro, F. Fujimoto, and G. Ardo

I—Formalised Film of Untreated PVA

J. Soc. Textile Cellulose Ind. Japan, **15** (March 1959) 218–222

No correlation is observed between the adsorption isotherm and degree of formalisation or temperature if $[D]_f$ is expressed as weight of dye adsorbed per unit weight of dry film. When expressed per unit weight of swollen film, the isotherms change systematically and consist of a Langmuir part and a constant partition section. The former is favoured by a small degree of formalisation.

II—Formalised Film of Heat-treated PVA

Ibid., 222–227

The distribution of the degree of formalisation within the fibre is measured. Adsorption isotherms are obtained and are similar to those obtained in I. L.P.

Effect of Dyeing on Permeability of Textiles to Ultraviolet Radiation
W. P. Zwelodub *Textil Praxis*, **14** (Sept 1959) 906–910

Preliminary conclusions from the results of an investigation into the influence of fabric dyeing on the permeability of ultraviolet radiation indicate that, in general, dyeing reduces penetration of ultraviolet rays of different wavelengths. Permeability is affected by the fabric structure but not by its colour. L.A.T.

Dyeing Woven Fabrics under the Influence of Electric Current
W. E. Rostowzew and R. M. Trachtenberg

Textil Praxis, **14** (Aug 1959) 807–810

Laboratory scale apparatus is described for continuous dyeing of woven fabrics. A.C. at 60–200 v. and 5–12 amp. passes through the contact rollers, bringing the dyebath to the boil and raising the temp. of the fabric to about 104°c. Consequently the rate of diffusion of the dye into the fibre is considerably increased and the dyeing time appreciably reduced. The consumption of electric current is related to fabric thickness and width, and the linear speed of the fabric through the bath. L.A.T.

PATENTS

Pad–Roll Dyeing
Rydboholms *BP* 817,134

Modification of *BP* 704,972 (J.S.D.C., **70** (1954) 209). The cloth is impregnated with dye liquor, heated to the temperature required to fix the dye, wound on to a roller in a chamber filled either with air saturated with moisture or with superheated steam, the temperature in the chamber being maintained higher than that at which the dye is fixed. The batched cloth is rotated in this atmosphere until the dye is uniformly distributed and fixed. Unlike the parent method it is unnecessary to maintain accurate control of the walls of the chamber to prevent condensation on them. C.O.C.

Colouring Cellulose Textiles with Water-soluble Dyes containing Sulphonamide Groups
ICI *BP* 823,098

Good colorations of good fastness to washing are obtained on cellulosic textiles by treating them with a dye containing at least one ionic solubilising group and at least one group of formula SO_2R (R = β-chloro- or β-bromo-ethylamino) in presence of an acid binding agent. Thus cotton cloth is padded with an aqueous solution of the dye *m*-aminobenzenesulphon - β - chloroethylamide→2 - amino - 8 - hydroxynaphthalene-6-sulphonic acid, dried at 50°c., passed through an aqueous solution containing 1% NaOH and 30% NaCl, steamed for 1 min. and rinsed in 4% aq. $NaHCO_3$ and then water. Finally it is washed for 5 min. at the boil in a 0·3% aqueous solution of an alkyl phenol-ethylene oxide condensate, rinsed and dried. The cloth is dyed brick red of excellent fastness to severe washing and other wet treatments. C.O.C.

Hair Dyeing
L. Peters and C. B. Stevens *BP* 826,479

The hair is treated with an aqueous solution or dispersion of an organic colorant and an organic solvent for the colorant. This solvent must be either insoluble or only slightly soluble in water and at the temperature of dyeing the colorant must be more soluble in the solvent than in water. Thus white human hair was dyed light brown by impregnating it with a mixture of C.I. Acid Brown 50 (2 parts), amyl lactate (2), and water (96) for 30 min. at 30°c. and washing with an aqueous solution of synthetic detergent to remove surplus colorant. C.O.C.

Dyeing Leather with Direct Dyes
General Aniline *USP* 2,893,811

Leather tanned with vegetable tanning extracts or with HCHO and a polyhydric phenol is readily dyed with direct dyes from an aqueous bath at pH 5·5–7·0 containing 0·1–5·0% (on wt. of leather) of a compound of formula—

$$R{\cdot}NH{\cdot}(CH_2CH_2O)_nH$$

(R = straight chain aliphatic hydrocarbon radical of 16–18 C; n = 12–18), e.g. condensate of 15 mol. ethylene oxide with 1 mol. of a mixture of 30% hexadecylamine, 25% octadecylamine, and 45% octadecenylamine. C.O.C.

Europe's Model Textile Finisher (Process Control at the Royal Twentsche Steam Bleachery) (I p. 190)
Affinity of Direct Dyes for Cellulose (IV p. 192)
Coloration of Cellulose by Application of Reactive Dyes and Intermediates Aftertreated with Diazo Compounds (IV p. 195)
Chlorophyll Contamination of Wool and its Effect on the Lightfastness of Dyeings (VI p. 198)
Mass-coloured Acrylic Fibres (VI p. 199)

IX—PRINTING

PATENTS

Colour Photographic Materials
ICI *BP* 818,687

Materials of improved speed are obtained if the sensitive layer nearest to the support is made up of two separate coatings of silver halide emulsions each containing non-diffusible colour formers which on development yield

images of the same colour and each sensitised to light of the same wavelength. C.O.C.

Basic and Acid Dyes for use in Photographic Anti-halation and Filter Layers

Agfa *BP* 818,639

Addition products of organic compounds containing an active methylene or methyl group with either (*a*) a basic dye non-resistant to alkaline silver halide developing solution containing sulphite, or (*b*) an acid dye (or its alkali metal, NH_4 or amine salt) obtained by condensing an *N*-substituted carbazole-3-aldehyde or indole-β-aldehyde, are very suitable for use in gelatin or other hydrophilic colloid for production of antihalation and filter layers. C.O.C.

Coloration of Cellulose by Application of Reactive Dyes and Intermediates aftertreated with Diazo Compounds (IV p. 195)

X—SIZING AND FINISHING

A Practical Approach to the Evaluation of a Finishing Agent

J. J. McDonald and R. E. Morrison

Amer. Dyestuff Rep., **47** (7 April 1958) 211–2

An account of a logical approach for the practical evaluation of a finishing agent. Application of a cationic agent to cotton, viscose rayon, and acetate rayon fabrics is described. The agent was applied to the fabrics alone, as part of resin treatments and to resin treated fabric. The treated fabrics were then evaluated. The evaluation included visual examination, tensile and tear strength, wrinkle recovery and abrasion tests. Effect of the agent on the resin solutions was also observed. The results obtained are detailed. W.P.M.

Polymers as related to Fabric Processing

D. D. Gagliardi, V. S. Frank, L. H. Perry, and H. F. Mark

Amer. Dyestuff Rep., **48** (1 June 1959) 37–42, 49

Verbatim account of a panel discussion at the AATCC Northern New England Section. Recent developments in use of polymers for durable textile finishes were summarised and discussed. Emphasis was laid on chlorine resistant wash and wear finishes, polymers of lower acrylic esters with functional groups which can react with a fibrous film or substrate, polyethylene imine and its use in cellophane and paper processing, the importance of the colloidal properties of aqueous dispersions of polymers (e.g. in antisoiling finishes) and the use of other functional groups besides formaldehyde, e.g. epoxy, ethyleneimine, and isocyanate. W.P.M.

Reaction of Epoxides with Cotton Cellulose in Presence of Sodium Hydroxide

J. B. McKelvey, B. G. Webre, and E. Klein

Text. Research J., **29** (Nov 1959) 918–925

Epoxides in which the ring is strained but unhindered by adjacent substituents, react with cellulose in presence of NaOH. The products may be single cellulose hydroxy ethers formed in presence of solvents, or linear graft polymers of the epoxide formed randomly and unevenly in the yarn in absence of solvent. The reactivity of the epoxides with cellulose is independent of their solubility in water because such water-insoluble epoxides as phenyl glycidyl ether and styrene oxide react as readily as some water-soluble epoxides. In considering the reaction mechanism account has to be taken of the maximum add-on obtained when the concentration of the caustic lye is varied, necessity for water to be present, and solubility of the epoxide in the lye. Probably the reaction is an S_N2 mechanism similar to that proposed by Lowry (*J.C.S.*, **127** (1925) 1371–1385). The properties of the products depend greatly on the hydrophilic–hydrophobic balance of the reacting epoxide. C.O.C.

Preparation and Properties of Partially Phosphonomethylated Cotton

S. R. Hobart, G. L. Drake, and J. D. Guthrie

Text. Research J., **29** (Nov 1959) 884–9

At sufficiently high phosphorus content fabric phosphonomethylated on a works finishing plant has a permanently starched handle and improved wet crease resistance. Good flame resistance is shown by the ammonium salt of the treated fibres. The treated fabrics are more hydrophilic than the controls. The phosphorus content is very stable to alkali. The copper salt of the treated fibres has considerable resistance to microbiological attack compared with untreated cotton. C.O.C.

Chemical Modification of Cotton—Aminisation Cost Study

O. J. McMillan, K. M. Decossas, G. L. Drake, J. D. Guthrie, and E. F. Pollard

Amer. Dyestuff Rep., **48** (24 Aug 1959) 37–8

Introduction of aminoethyl groups into cotton makes the fibre more reactive so that it readily undergoes further modification whereby flame and rot resistance, water repellency and other useful properties may be imparted to it. Aminisation also confers upon cotton high affinity for wool dyes. Preliminary cost studies for continuous production of aminised cotton show that it can be produced in large quantities at relatively low cost (20·4 cents per lb. for 0·6% N content exclusive of fabric cost) as the reagents are readily available and cheap and the process may be carried out on conventional textile equipment. W.P.M.

Cross-linking of Partly Cyanoethylated Cotton
Part I—Carbamoylethylation and Formaldehyde-curing

M. Negishi and N. Aida

Text. Research J., **51** (Dec 1959) 982–9

Using the hydrogen peroxide method enabled partly cyanoethylated cotton containing a low percentage of N to be carbamoylethylated with almost no damage. Formaldehyde-curing (110–150°C.) in presence of an acid catalyst, e.g. NH_4 or dimethylaniline hydrochloride, imparted crease recovery properties, accompanied by corresponding loss in tensile strength and elongation, better than those of the cyanoethylated cotton. However, the improvement was less than that with unmodified cotton. Curing at 110–130°C. with a moderately weak acid catalyst, e.g. secondary ammonium phosphate, improved the crease recovery properties to some extent with much less decrease in tensile strength and elongation. This suggests that in the formaldehyde-curing of partly carbamoylethylated cotton fabrics a long chain *N*-methylenebisethyleneamide cross linkage is formed between different cellulose molecules. Ammonium acetate was not a powerful enough catalyst. The good dyeing properties of cyanoethylated cotton are retained after carbamoylethylation and formaldehyde curing.

Part II—Formaldehyde-curing After Amidoximation

M. Negishi, H. Ito, and N. Aida *Ibid.*, 990–5

Cyanoethylated cotton cloth when amidoximated by treatment with aqueous hydroxylamine and then formaldehyde-curing in presence of a weak acid catalyst, e.g. NH_4 acetate, or even in absence of a catalyst, has improved crease recovery properties without much decrease in tensile strength and elongation but with some decrease in flex abrasion and tear strength. Probably intermolecular cross links are formed between adjacent amidoxime or hydroxamic acid groups in different cellulose molecules. The cured cloth has the good affinity for acid dyes and the wool-like handle of the original cyanoethylated cotton cloth. C.O.C.

Wrinkle Resistant Cotton with Durable Chlorine Resistance

J. G. Frick, P. J. Murphy, R. T. M. Reinhardt, R. L. Arceneaux, and J. D. Reid

Amer. Dyestuff Rep., **48** (7 Sept 1959) 37–40

Application, to cotton, of mixtures of dimethylol urea and formals (from formaldehyde and either diethylene glycol or pentaerythritol) and evaluation of the finishes obtained, is described. The finishes had good wrinkle and chlorine resistance both of which were fast to repeated laundering; but they are susceptible to excessively hot acid souring conditions. $Zn(NO_3)_2$, and not $MgCl_2$, is the preferred catalyst because less durable chlorine resistance is obtained with the latter. With $Zn(NO_3)_2$ curing conditions must be carefully controlled to avoid yellowing. Increased tear strength, crease recovery and "wash and wear" properties were achieved by addition of a polyethylene softening agent. W.P.M.

Performance of Selected Resin-treated Percales

J. Golden, H. T. Stevens, and H. L. Richey

Amer. Dyestuff Rep., **48** (24 Aug 1959) 29–35

Percales having three finishes ("minimum care", wrinkle resistant, and Sanforized) were studied under

controlled and uncontrolled laundering methods, 69 skirts made from the fabrics were worn for 20 weeks (10 launderings). Routine analyses and appearance tests were carried out on the fabrics after 1, 3, 5, and 10 launderings. Results showed differences existing between objective and subjective measurements. Objectively measured differences in wrinkle recovery values of the resin-treated fabrics were not compatible with visual differences as indicated by appearance scores. With repeated launderings the resin-treated fabrics decreased in wrinkle recovery; visual differences were not discernible. Much ironing time was saved by resin treatment, the "minimum care" fabrics needing least ironing. High incidence in use of moisture (principally sprinkling) in the home ironed resin-treated fabrics indicates a lag in consumer practices over manufacture recommendations.
W.P.M.

Copper Formate as a Rotproofer for Cotton
G. R. F. Rose, J. B. Howdon, and C. H. Bagley
Text. Research J., **51** (Dec 1959) 996–1005

Impregnating cotton cloth with cupric formate to give a Cu content of ≮ 0·4% and then heating yields a fabric having considerable resistance to actinic degradation and microbiological attack. Heating should be done in an autoclave as heating in an ordinary drying chamber causes chemical degradation presumably by the combined action of heat and the liberated formic acid. The protection given is caused by presence in the fabric of cuprous oxide. Any copper compound not containing a potentially nutritive anion can replace the Cu formate to give equally good results. Cu formate has the advantage over other organic Cu compounds that it decomposes to yield inorganic Cu compounds, mostly Cu_2O, while the organic anion decomposes to gaseous compounds. C.O.C.

Some Factors Involved in Wash and Wear Wool
J. F. Krasny, H. E. Harris, G. H. Lourigan, and E. D. White *Amer. Dyestuff Rep.*, **48** (7 Sept 1959) 31–6

Evaluation of wash and wear characteristics of a range of commercial wool fabrics, on a basis of shrinkage, mussiness and fuzz formation on laundering, is described. Several of the fabrics, because of their construction, are reasonably dimensionally stable in machine laundering followed by air or tumbler drying. Fabrics which showed some shrinkage in air shrank more on tumbler drying. In some fabrics a considerable increase in surface fuzziness was observed after laundering. Chlorination reduced both shrinkage and formation of fuzz in laundering and tumbler drying. Most fabrics had satisfactory wash and wear properties by the present standard for cellulose fabrics.
W.P.M.

Factors affecting the Drying of Apparel Fabrics. Part III—Finishing Agents
R. Steele *Text. Research J.*, **51** (Dec 1959) 960–6

Finishes can affect drying time only by changing the amount of water held by the wet fabric. Water repellents, reactive cross-linking resins, and surface polymers all reduce the water-holding capacity of fabric to various degrees. However, water repellents show no effect if mechanical agitation or a surface-active agent is used in wetting the fabric. The 20–30% reductions in water-holding capacity caused by reactive and surface resins are not affected by either of these factors. C.O.C.

PATENTS

Water-repellent Finish Fast to Washing and Dry Cleaning
Calico Printers' Assocn. *BP* 818,492

Animal or vegetable fibres, natural or regenerated, are treated with derivatives of 1,3,5-triazine having at least one Hal and at least one –NHAlk (Alk of > 10 C) group substituted on C atoms and containing no solubilising group, preferably in presence of an acid binding agent. Thus cotton cloth was impregnated with 130% of its weight of 15% aq. Na_2CO_3 and dried. It was then padded through a 2·5% solution of 2-stearylamino-4,6-dichloro-1,3,5-triazine in chloroform to an expression of 117%. After removal of the chloroform the cloth was steamed for 30 min. and finally washed in hot water for 10 min. The treated cloth had an excellent water repellent finish which was improved by washing in hot soap solution and was fast to dry cleaning in trichlorethylene. C.O.C.

Rotproofing Composition
Monsanto Chemical Co. *USP* 2,893,881

When cellulosic materials are impregnated with a volatile solvent solution of a chlorinated phenol or chlorinated hydrocarbon addition of a water-insoluble phosphoric ester increases the solubility of the chlorinated phenol and retains it in a more stable form. This results in the treated material being given a better rotproof finish. C.O.C.

Cloth having Exceptional Resistance to Wear
Riegel Textile Corpn. *USP* 2,893,315

A thermoplastic composition of high viscosity is doctored through a cylindrical screen on to the cloth. The composition has such thixotropic properties that it readily passes through the screen but does not penetrate below the surface of the cloth.

USP 2,893,314

The composition is applied to the cloth according to a predetermined pattern. C.O.C.

Water-repellent Finish (III p. 191)
Bonding Agents for making Bonded Fibre Fabrics (III p. 191)
Cross-linking of Wool by Aldehydes. II—Mechanism of Cross-linking (VI p. 199)
Migration of Liquids in Textile Assemblies. Part II—Wicking of Liquids in Yarns (VI p. 199)
Continuous Wet-processing of Cotton–Acrilan Work-clothing Fabrics (VIII p. 201)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Should the Brightness of a Pulp be Measured on Pulp Machine Sheets or on Laboratory Sheets?
C. Valeur
Svensk Papperstidning, **62** (31 Dec 1959) 915–919 (in English)

Brightness is affected by compression of the sheet (brightness decreases with increasing pressure), degree of drying, and ageing. In addition, the differences between laboratory and machine sheets may vary with the time of the year, probably because the warmer water in summer gives higher compression in the wet presses. Brightness measurements on pulp machine sheets have limited value and should only be used as a routine control in pulp mills where the pulp is pressed and dried under constant conditions. Even then the true brightness level must be checked regularly by measurements made on laboratory sheets. R.A.

Carbon Paper (V p. 198)
Effect of Pulp History on Pulp Response during Hypochlorite Bleaching (VII p. 200)
Distribution of Oxidant Consumption in Bleaching (VII p. 200)

XIII—RUBBER; RESINS; PLASTICS

Sorption of Congo Red by Polyvinyl–Formal (VIII p. 202)
Polymers as related to Fabric Processing (X p. 203)

XIV—ANALYSIS; TESTING; APPARATUS

PATENT

Testing Solids, Liquids or Gases for Presence of Substances forming Azo Dyes
VEB Leuna-Werke "Walter Ulbricht" *BP* 818,845

Apparatus for the continuous testing of solids, liquids or gases for presence of substances forming azo dyes, e.g. for testing effluents for presence of phenols. C.O.C.

Dry Weight of Wool (VI p. 198)
Migration of Liquids on Textile Assemblies. Part II—Wicking of Liquids in Yarns (VI p. 199)
A Practical Approach to the Evaluation of a Finishing Agent (X p. 203)
Should the Brightness of a Pulp be Measured on Pulp Machine Sheets or on Laboratory Sheets (XI above)

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